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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2944. **Analytical properties of anthranilic acid and its derivatives.** W. F. Harris (Ohio State Univ., U.S.A.). *Dissert. Abstr.*, 1956, **16** (3), 441.—In order to investigate the pH ranges for pptn. of Cu, Ni, Co, Zn and Cd with anthranilic acid from acetate buffers, rapid and accurate volumetric methods for determining the metal in the ppt. were developed. In general, the ppt. was dissolved in HCl and the soln. evaporated almost to dryness. For Ni and Cu the solutions were made basic with aq. NH_3 and titrated with a standard EDTA soln., murexide being used as the indicator; Eriochrome black T was used as the indicator for Zn. For Co and Cd, an excess of EDTA was added before making the soln. basic. The excess of EDTA was titrated with standard zinc soln.; Eriochrome black T was used as indicator. The formation constants of Cu and Cd in 50 per cent. dioxan with anthranilic acid and the N-methyl, N-phenyl, 3:5-di-iodo, 3-methyl and 5-sulpho derivatives, and of Cu, Ni, Co, Zn and Cd with 5-sulpho-anthranilic acid in H_2O and with NN′-ethylenedianthranilic acid in 50 per cent. dioxan were determined. O. M. WHITTON

2945. **Quinol, a new reductimetric reagent.** V. Simon and J. Zýka (Inst. anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (2), 327–338.—Quinol is a stable volumetric reducing agent, even in 0·001 *N* soln. The soln. is readily standardised against $K_2Cr_2O_7$ and diphenylamine. Quinol can be used for the volumetric estimation of halogens, active chlorine, BrO_3', IO_3', $[Fe(CN)_6]'''$, Au^{III}, Cr_2O_7'', VO_3' and Ce^{IV}. An excess of Fe does not interfere, since Fe^{III} is not reduced by quinol. The end-points are detected potentiometrically, although in some cases the use of diphenylamine or ferroin is possible. In most instances the methods can be adapted for micro-analysis. Methods are described for the estimation of Cr and V in steels, either alone or in the presence of each other. J. H. WATON

2946. **The use of alkali hydroxides for the separation of the copper and arsenic groups in qualitative inorganic analysis.** A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester (Woolwich Polytechnic, London, England). *Analyst*, 1956, **81**, 244–245.—Holness *et al.* (*Brit. Abstr. C*, 1950, 470) have claimed certain advantages in the use of a 1 per cent. aq. soln. of LiOH containing 5 per cent. of KNO_3 for separation of the copper and arsenic groups in qual. inorganic analysis. James *et al.* (*Anal. Abstr.*, 1955, **2**, 1227) conclude that LiOH possesses no peculiar merits in comparison with NaOH and KOH, that Hg must be sought in groups 2A and 2B, that Sn^{**} should be oxidised before pptn. and that 0·5 *N* KOH is most suitable for the separation. The opinion of James *et al.* is now confirmed, but 2 *N* KOH is recommended. Since the soln. of SnS in KOH contains thiostannite and stannite, it is a powerful reducing agent and it is thus essential to oxidise Sn^{II} to Sn^{IV} with H_2O_2 or Br. If the amount of H_2O_2 is not excessive, little oxidation of Sb and As occurs. A. O. JONES

2947. **Influence of organic bases on the partition of indicator acids (and vice versa) in a water-chloroform system. Analytical applications.** G. N. Thomis and A. Z. Kotionis (Manuf. de Mat. Col. d'Athènes, Greece). *Anal. Chim. Acta*, 1956, **14** (5), 457–465.—The partition of bromothymol blue between $CHCl_3$ and water is influenced in favour of the organic layer by the addition of procaine, but increase of the pH of the aq. layer exerts a counter-influence. The partition of procaine is similarly affected by the addition of bromothymol blue, but decrease of pH favours extraction into the aq. phase. These effects are due to the formation of $CHCl_3$-sol. "amphi-indicators" (*cf. Anal. Abstr.*, 1956, **3**, 1603). When equimol. proportions of the base and bromothymol blue are present, and when the pH is $\simeq$ 6, the aq. layer contains no indicator, but a yellow colour is produced in the aq. layer as soon as a small excess of bromothymol blue is added. This affords a method for titrating procaine and other bases, *e.g.*, ephedrine, atropine, quinidine and strychnine. A soln. (0·2 ml) of the base, mixed with 2 ml of buffer soln. (pH 5·5) and 15 ml of $CHCl_3$, is titrated with 10^{-3} *M* bromothymol blue, vigorous shaking being applied between additions. The end-point is marked by a yellow colour in the aq. layer. This titration is used as an approx. determination. An accurate determination is then made by adding an excess of 4×10^{-4} *M* bromothymol blue to the soln. ($\Rightarrow 2 \times 10^{-4}$ *M*) of the base, buffered at pH 7·5, extracting with $CHCl_3$ and determining the bromothymol blue in the $CHCl_3$ layer by extracting it with aq. NaOH and comparing the colour of the alkaline extract with standards. These principles are used in the determination of alkaloids and other basic drugs in some pharmaceutical preparations. Other indicators are also brought into similar use. W. C. JOHNSON

2948. **The application of ion-exchange resins to the preparation of standard acids.** C. J. Keattch (Northern Polytechnic, London). *Lab. Practice*, 1956, **5** (6), 208–209.—Standard solutions of HCl, H_2SO_4, HNO_3 and acetic acid were prepared by weighing out an appropriate salt, dissolving it in H_2O, passing the soln. through a cation-exchange column and making the eluate up to a known volume. Details of the method and some results are given. The upper limit of concn. recommended for solutions prepared by this method is 0·25 *N*.
O. M. WHITTON

2949. **Saturated barium iodate solutions as iodimetric standards.** S. K. Yasuda and J. L. Lambert (Kansas State Coll., Manhattan, U.S.A.). *Chemist Analyst*, 1956, **45** (2), 50–51.—The preparation of

standard solutions of iodate of the order of 0·01 *N*, accurate to three significant figures, is described. Distilled H_2O is saturated at constant temp. with $Ba(IO_3)_2.H_2O$ (**I**), either by stirring an excess of **I** (0·1 g) with H_2O (100 ml) in a constant-temp. water bath at 25° C for about 1 hr., or more conveniently by passing H_2O through a column of **I** contained in a 50-ml burette. Soln. obtained by each procedure were analysed by titration of the I liberated through reaction with excess of iodide and acid. Gravimetric determination of the Ba in 0·5-g samples of **I** by pptn. and ignition as $BaSO_4$ indicated 100·2 per cent. purity. Titration of I liberated by reaction of **I** with I′ in excess of acid indicated 99·9 per cent. purity. Attempts to prepare strontium iodate and lead iodate by the periodate method were unsuccessful.

O. M. WHITTON

2950. **Diethylenetetra-ammonium sulphatocerate [ceric ethylenediamine sulphate] as volumetric reagent. II. Iodine monochloride method. Indirect determinations.** Balwant Singh and Surgit Singh (Punjab Univ. College, Hoshiarpur, India). *Anal. Chim. Acta*, 1956, **14** (5), 405–408.—The reagent affords indirect titrations of the following substances—KIO_3, KIO_4, $K_2Cr_2O_7$, $KBrO_3$, $Ce(SO_4)_2$, H_2O_2, PbO_2 and chloramine B. *Procedure*—To the sample soln. in a stoppered flask add 5 ml of $CHCl_3$, an excess of 0·02 *N* KI and sufficient conc. HCl to maintain a HCl concn. of 4 to 6 *N*. Titrate the excess of KI with a 0·02 *N* soln. of the reagent, shaking the flask vigorously after each addition, until the colour of the $CHCl_3$ layer changes from violet to pale yellow. W. C. JOHNSON

2951. **Interferometric titrations and their applications. I.** F. Burriel-Martí and M. Claver Aliod (Inst. de Edafología del C.S.I.C., Madrid). *Inf. Quim. Anal.*, 1956, **10** (2), 39–49.—The titration of solutions of NaCl and KI with $AgNO_3$, determining the end-point from the change in refractive index of the colloidal solution, is described. Satisfactory results have been obtained with 10^{-2} to 10^{-3} *N* NaCl and 10^{-5} to 10^{-6} *N* KI. This method may be used for the determination of NaCl in soils after calcination, aq. extraction, pptn. of metal hydroxides with aq. NH_3 and elimination of NH_3.

L. A. O'NEILL

2952. **Analytical application of complexones. IV. Gravimetric determinations and analytical separations.** F. Bermejo Martínez and A. Prieto Bouza (Univ. Santiago de Compostela, Spain). *Inf. Quim. Anal.*, 1956, **10** (2), 50–59.—Applications of complexones to improve the selectivity of gravimetric precipitations are reviewed, *viz*, in the determinations of As, Al, Ba, Be, Bi, Ca, Cu, Sn, P, Fe, Hg, Mo, Ni, Ag, K, Ti, U, W, SO_4'' and guanidine. L. A. O'NEILL

2953. **Complexometric titrations. XIV. Zinc dipyridine dithiocyanate as standard in complexometric titrations.** B. Buděšínský (Pharm. & Biochem. Res. Inst., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (1), 255–257.—The preparation of zinc dipyridine dithiocyanate $[Zn(C_5H_5N)_2](SCN)_2$ in a pure state is described. The compound is said to be particularly suitable because of its purity, stability and high equivalent for the standardisation of EDTA. The end-point, with Eriochrome black T or murexide as indicator, is very good. P. S. STROSS

2954. **Catechol violet: indicator for chelatometric titrations.** V. Suk and M. Malat (Karlova Univ., Prague, Czechoslovakia). *Chemist Analyst*, 1956, **45** (2), 30–37.—The properties of the indicator catechol violet and its applications, including chelatometric titrations, are reviewed. Procedures are described that illustrate its use in the determination of Bi; of Bi in the presence of $Fe^{\cdots}$ and $Hg^{\cdot\cdot}$; of Th, Cu, Fe, Al, Ti, Pb, Ga, Ni, Pd, Co, Mn, Zn, Mg and Cd; and in the indirect determination of In, Ga, Fe, Bi and Th. These involve titration with standard EDTA soln.

O. M. WHITTON

2955. **Use of pyrogallolcarboxylic acid as compleximetric indicator.** M. Kovařík and M. Moučka (Montan-Hochschule, Ostrau, Czechoslovakia). *Z. anal. Chem.*, 1956, **150** (6), 416–420.—Pyrogallolcarboxylic acid (**I**) is used as indicator in the determination of Ca by titration at pH 12 with EDTA. The method is suitable for the determination of Ca in drinking water, after removal of heavy metals with Na_2S. No interference is caused by Mg. For other cations (Ba, Sr, Pb, Cd, Al and Zn), direct titration is inadvisable (indistinct colour change) and these ions are determined by addition of excess of EDTA and back-titration with $BaCl_2$. The method is highly accurate and of general applicability to metals forming colourless and stable EDTA complexes at pH 12. *Procedure*—For the determination of Ca, adjust the soln. of Ca salt to pH 12 (or higher), add a satd. aq. soln. of **I** (one-tenth of total vol.), and titrate with 0·1 *M* EDTA. At the end-point the violet colour disappears. For the determination of other metals, add to the soln. of the metal salt a measured excess of 0·1 *M* EDTA, adjust to pH 12, add the satd. aq. soln. of **I**, and titrate with 0·1 *M* $BaCl_2$. At the end-point the colour changes from yellow to violet.

J. P. STERN

2956. **Ion exchangers in analytical chemistry: applications and problems.** O.-E. Schultz (Pharm. Inst. Univ. Kiel, Germany). *J. Pharm. Pharmacol.*, 1956, **8** (6), 382–396.—This is a review, with 108 references, of the application of ion-exchange resins to qualitative and quantitative inorganic analysis; the micro-determination of acetyl groups, aldehydes, ketones and metals; the assay of alkaloids, glycosides and reducing sugars in plant extracts; and the analysis of local anaesthetic, sympathomimetic, spasmolytic, cough-sedative and antihistaminic drugs, amino acids, vitamins and antibiotics. A. R. ROGERS

2957. **Technical applications of ion exchange.** J. Büchi (Pharm. Inst., Zurich, Switzerland). *J. Pharm. Pharmacol.*, 1956, **8** (6), 369–381.—The batch, column and membrane techniques of using ion-exchange resins are described. A review is given of the use of ion-exchange resins for the removal of undesired foreign ions or electrolytes from preparations (*e.g.*, water, glycerol, enzymes), the concentration of desired ions or electrolytes (*e.g.*, alkaloids, vitamins, antibiotics, amino acids), and the catalysis of reactions. A. R. ROGERS

2958. **Complexone exchange resins: preparation and uses.** E. Blasius and G. Olbrich (Anorg.-Chem. Inst., Tech. Univ., Berlin-Charlottenburg, Germany). *Z. anal. Chem.*, 1956, **151** (2), 81–90.—The preparation of a resin from *m*-phenylenediaminetetra-acetic acid, resorcinol and formaldehyde is described. The acid form of the resin is

used for the separation of metal cations by varying the pH of the eluent in a chromatographic procedure. Thus 0·1-milli-equiv. quant. of the alkali or alkaline-earth metals and Cu or Ni can be separated on a column (25 cm × 2·2 cm) by elution of the former with 0·01 *N* HCl and the latter with 2 *N* HCl; recoveries range from 99·6 to 100·4 per cent. The separation of Co and Ni can be achieved, but conditions, such as the rate of elution, are critical. A. R. ROGERS

2959. **Paper electrophoresis of several anions.** Hideo Nagai and Shigehiro Kurata (Dept. of Chem., Faculty of Sci., Kumamoto Univ., Kumamoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (3), 451–454.—An experiment similar to that for Cl′, Br′ and I′ (*cf.* Ohara and Nagai, *Anal. Abstr.*, 1956, **3**, 107) was carried out with $Fe(CN)_6'''$, $Fe(CN)_6''''$, SCN′, Cr_2O_7'' and PO_4'''. When a mixture of the potassium salts of these anions is submitted to electrophoresis (300 V) in dil. lactic acid, the distance of migration of the spots increases linearly with time; the spots become more diffused with decreasing concn. of the lactic acid. Simultaneous detection of these anions (except Cr_2O_7'', which decomposes during development) can be effected in *M* lactic acid within 1 hr. by the use of ammoniacal $AgNO_3$ as revealing agent. K. SAITO

2960. **Bibliography on analytical flame spectroscopy. I.** R. Mavrodineanu (Boyce Thompson Inst. Plant Res., Inc., Yonkers, N.Y., U.S.A.). *Applied Spectroscopy*, 1956, **10** (2), 51–64.—A brief historical introduction is followed by a bibliography arranged chronologically, in alphabetical order of authors, covering the years 1848 to 1951. A subsequent paper will complete the bibliography up to 1955 and will include a subject index. P. T. BEALE

2961. **Application of spot-test techniques to fluorimetric analysis.** J. R. Wiebush (Univ. of Maryland, Md., U.S.A.). *Dissert. Abstr.*, 1956, **16** (1), 20.—Fluorimetric reagents suitable for paper spot-tests with eight elements are as follows—Al (acid alizarin garnet R, colour index 168); Ga (Eriochrome red B, colour index (652); Ga (8-hydroxyquinaldine); Zr (quercetin); Sn (quercetin); fluoride (Zr - quercetin complex); fluoride (Al - acid alizarin garnet R complex); Zn (8-hydroxyquinaldine); B (benzoin or quercetin); Ge (2-salicylideneaminophenol). The reagents are highly selective and sensitivity is of the order of 1 μg per 0·01-ml drop. The high-pressure mercury-vapour lamp with max. emission wavelength of 365 mμ proved to be the most practical intense source of excitation for the fluorescence of metal chelates. A fluorimetric determination of Ga in the presence of Al, with Eriochrome red B as the reagent, was devised; at pH 2 (obtained by using 2·5 *N* acetic acid) only the gallium chelate forms, whereas at pH 4 both Al and Ga form fluorescing chelates. G. HELMS

See also Abstracts 3083, 3084.

2.—INORGANIC ANALYSIS

2962. **Nitrometry of inorganic salts. I. Determination of trace amounts of metals that form insoluble oxinates.** Kiyoshi Takiura, Yoshio Takino and Chiyoko Tange (Pharm. Inst., Medical Faculty, Osaka Univ., Hotarugaike, Toyonaka, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (6), 724–726.—Metals that form insol. oxinates (Al, Bi, Ca, Cd, Co, Cr, Cu, Fe, La, Mn, Mg, Ni, Pb, Th, Ti and U) are indirectly determined by the nitrometric determination of the nitrogen in the oxinates (error < 1 per cent.). The metal oxinates (≃ 0·0001 mole) are pptd. by the usual method, washed with ammonium acetate soln. of appropriate pH value and dissolved in 2 *N* HCl (50 ml). A 1-ml portion is treated with 0·0025 *M* $KBrO_3$ (in 0·5 *M* KBr) (1 ml) to brominate the oxine and transferred to a nitrometer with KI (1 g). The air in the nitrometer is replaced with CO_2 and the soln. is treated with hydrazine sulphate (750 mg in 100 ml of 10 *N* NaOH, containing 0·5 ml of octanol to minimise foaming) (1 ml). The liberated nitrogen is measured volumetrically. Any Cr^{III} should be reduced to Cr^{II} with hydroxylamine before the pptn. of its oxinate. K. SAITO

2963. **Separation and identification of some elements whose chlorides are extractable with ethyl acetate.** R. Vanossi. *An. Asoc. Quim. Argent.*, 1955, **43** (3), 151–172.—A scheme is given for the separation of Au, Th, Te, Fe, Mo and Ga from other metals by extraction of their chlorides with ethyl acetate from an aqueous 4 *M* HCl solution. On partial neutralisation of the HCl to 0·5 *M*, Au and Th^{III} remain in the solvent whilst the remaining chlorides pass into the aqueous phase. L. G. L. UNSTEAD-JOSS

2964. **Liquid - liquid extraction procedures in inorganic analysis. I.** T. S. West (Univ. Birmingham, England). *Metallurgia, Manchr*, 1956, **53**, 91–96.—The general principles of solvent-extraction procedures are reviewed, with particular reference to metallurgical analysis. Extraction procedures for Cu as Cu^{II} - dipyridine dithiocyanate and as Cu butyrate, with acetylacetone and as a complex with neocuproine (2:9-dimethyl-1:10-phenanthroline) and methods for Ag and Au are discussed. (23 references.) S.C.I. ABSTR.

2965. **The analytical application of heterocyclic pigments. I. The coloration developed between 5:8-dihydroxyquinoxaline and several metal ions.** Sin'iti Kawai, Hiroshi Hamaguchi and Mitsunobu Tatsumoto (Dept. of Chem., Faculty of Sci., Tokyo Univ. of Educ., Koishikawa, Tokyo). *Japan Analyst*, 1956, **5** (3), 165–169.—The use of 5:8-dihydroxyquinoxaline (**I**) (Adachi, *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76**, 311) for both qual. and quant. determination of heavy-metal ions was studied under various conditions. An orange to red colour is given by Ga, In, $Tl^{\cdots}$, $Pb^{\cdot\cdot}$, $U^{\cdots\cdots}$, MnO_4'' and WO_4'' in a weakly acid soln., whilst blue ppt. are given by Cd, Co, Cu, $Fe^{\cdot\cdot}$, Ni and Zn. These ppt. are not readily sol. in org. solvents and appear to have a polymeric structure, as suggested by Kawai *et al.* (*Proc. Japan Acad.*, 1953, **29**, 344). Under certain conditions **I** reacts only with Cu and can be used for its colorimetric determination. K. SAITO

2966. **A note on the conditions for obtaining chromatograms of cations on alumina for estimation from the dimensions of zone.** T. K. Meenakshisundaram and B. S. Srikantan (Stanley Med. Coll., Madras, India). *J. Indian Chem. Soc.*, 1955, **32** (12), 801–802.—Directions are given for the preparation of an alumina column for the quant. determination of cations ($Cu^{\cdot\cdot}$) from the dimensions of the zone. Estimations in which standard solutions

of $CuSO_4$, $Cu(NO_3)_2$ and $CuCl_2$ are used are carried out under similar conditions; $Cu(NO_3)_2$ gives the longest band for the same amount of Cu^{++}, and its use is recommended for accurate determinations.

I. JONES

2967. **Spectrochemical determination of small inclusions in minerals by means of high-frequency excitation.** A. Maucher and S. Auerhammer (Inst. f. allg. u. angew. Geol. u. Mineral., Univ. Munich). *Mikrochim. Acta*, 1956, (1–3), 401–405.—Emission spectral analysis offers one of the best microchemical techniques for the identification of small inclusions weighing < 1 mg and with a cross-section $< 0{\cdot}5$ mm, especially when it is necessary to avoid contamination from the surrounding material. A source unit is described which is a combination of a high-frequency spark and d.c. arc with a stabilising device based on the principles of W. Gerlach *et al.* and of H. Triché. The device allows for a wide range of excitation conditions together with short exposures of from 10 to 30 sec. and an area of attack of < 1 mm cross-section. By boring a hole in the polished section of a mineral, a conductor can be led to the inclusion with a 0·5-mm platinum wire serving as the counter electrode. Should Pt be the element sought, then some other counter electrode is selected. A grating spectrograph is used with a mean dispersion of 5·5 A per mm.

D. F. PHILLIPS

2968. **Applications of flame photometry to the determination of elements other than alkalis or alkaline earths.** F. Burriel-Martí, J. Ramírez-Muñoz and M. C. Asunción-Omarrementería (Fac. Sci., Univ. Madrid, Spain). *Mikrochim. Acta*, 1956, (1–3), 362–381.—Although universally accepted for the determination of Na, K and Ca in biological or mineral samples, flame-photometry techniques are not so frequently used for the determination of other elements. The three factors preventing determination of metallic elements by such methods are—(*i*) low sensitivity in the flame; (*ii*) the presence of elements giving band spectra; (*iii*) the presence of major constituents that interfere with the emission of the element sought. The determination of Co, Ni, Cr and Mn in ferrous alloys has been studied by means of flame photometry. The sensitivity of these elements in the flame is low and their emissions are affected by the high concentration of Fe. Consequently Fe should be removed by preliminary separation with organic solvents. Procedures are described for preparation of steel samples, including preliminary separation of Ni with dimethylglyoxime. Results are reported for Ni, Co, Mn and Cr in steel, and for Mn in ferromanganese, and are compared with results obtained chemically. Although the precision and accuracy of the flame-photometer method are less satisfactory than with chemical methods the errors are within those expected for flame photometry. Advantages claimed are rapidity, the possibilities of dealing with large numbers of samples, reduction in number of prior chemical separations and simultaneous determination of several elements in the same soln. Interferences due to the presence of HCl are eliminated by the use of H_2SO_4.

D. F. PHILLIPS

2969. **Spectrochemical analysis of small samples.** E. Preuss (Inst. f. allg. u. angew. Geol. u. Mineral., Univ. Munich). *Mikrochim. Acta*, 1956, (1–3), 382–392.—By using the cathode arc layer of Mannkopff and Peters it is possible to make both qual. and quant. analyses of samples, *e.g.*, mineral granules, of the order of 1 to 30 μg. A large dispersion quartz spectrograph must be used in order to minimise the background to line ratio. In qual. work special consideration must be given to the manner in which the arc is projected in accordance with the light-emitting properties of the elements sought. Limits of detection with certain analysis lines under the stated conditions are quoted. In quant. analysis, special calibration curves must be prepared to compensate for the diverse self-absorptions and self-reversals of the analysis lines, which may vary according to the quantity of substance and unequal rates of volatilisation. It is recommended that control of these relationships is best achieved through determining self-absorption by comparison of the multiplets. By this means information can be obtained on the mean vapour pressure in the arc. An example of the establishment of calibration curves for the evaluation of from 5 to 50 per cent. of Ni in Ni - Fe alloy granules weighing from 10 to 30 μg is given.

D. F. PHILLIPS

2970. **Polarographic half-wave potentials of metal ions in various supporting electrolytes. I.** J. W. Grenier and L. Meites (Yale Univ., New Haven, Conn., U.S.A.). *Anal. Chim. Acta*, 1956, **14** (5), 482–494.—Data on the polarographic half-wave potentials, wave characteristics, probable reduction products and other polarographically important information are tabulated for 28 metal ions in nine supporting electrolytes containing hydrazine, pyridine, NaOH, KSCN, and pyrophosphate.

W. C. JOHNSON

2971. **Analytical applications of the Barker square-wave polarograph. II. The analysis of copper-base alloys and steels.** D. J. Ferrett and G. W. C. Milner (A.E.R.E., Harwell, England). *Analyst*, 1956, **81**, 193–203.—The application of the square-wave polarograph to the determination of some of the constituents of steel and copper-base alloys is described. In copper-base alloys, Sn is removed as its volatile bromide, and after solution of the residue in alkaline NH_4Cl - aq. NH_3 buffer soln. the polarograms of Zn and Ni are recorded in the presence of Na_2SO_3 soln. and compared with those from standard soln. For the determination of Pb after removal of Sn, the residue is fumed with HNO_3 and $HClO_4$ and the polarogram is recorded in a base soln. of KCN - NaOH - Na_2SO_3. The lead peak is recorded before and after addition of a known amount of a standard lead soln. and the Pb is thus determined. For the determination of Cu in steels, the sample is dissolved in HCl, fumed with HNO_3 and $HClO_4$, treated with HCl and diluted with water. The polarogram of an aliquot is recorded and the Cu is determined by the standard-addition method. Lead and Sn are determined similarly. Chromium is determined after oxidation to chromate with $(NH_4)_2S_2O_8$ in the presence of a trace of $AgNO_3$, the chromium peak being recorded from an alkaline mannitol base soln.

A. O. JONES

2972. **Determination of hydrogen in liquids and suspensions by nuclear magnetic absorption.** T. M. Shaw and R. H. Elsken (Southwest Res. Inst., San Antonio, Texas, U.S.A.). *Anal. Chem.*, 1955, **27** (12), 1983–1985.—The measurement of $D_{max.}$, the max. observed signal obtained in nuclear magnetic resonance absorption, provides a means for determining N_0, the no. of hydrogen nuclei per ml, in liquids and suspensions with hydrogen in the liquid phase. The effect of radio-frequency saturation is

overcome by measuring $D_{max.}$ at various values of the radio-frequency field H_1, plotting $D_{max.}$ against H_1^2, and obtaining $(D_{max.})_0$ by extrapolating back to $H_1^2 = 0$. Both for organic liquids and starch suspensions of varying water content, the ratio $(D_{max.})_0$ to N_0 is approx. constant. The method gives results with an error of ± 2 per cent. (absolute) when used to calculate the water content of starch suspensions, and might enable the moisture content of other hygroscopic materials, such as vegetable tissues, to be determined. J. H. WATON

2973. **Catalysis of hydrogen peroxide - hydriodic acid reaction by tungstate ions.** B. K. Shukla and J. V. S. Ramanjaneyulu (Central Salt Res. Inst., Bhavnagar, India). *Z. anal. Chem.*, 1956, **151** (1), 28–30.—The reaction between H_2O_2 and HI, which is used for the determination of H_2O_2, is catalysed by sodium tungstate. In the presence of this catalyst (three drops of 20 per cent. soln.), 5 ml of 2-vol. H_2O_2 in 50 ml of soln. (containing 5 ml of 3·6 *N* H_2SO_4 and 10 ml of 5 per cent. KI soln.) can be titrated with $Na_2S_2O_3$ within 15 min., whereas the uncatalysed reaction is incomplete after 30 min. The use of a large excess of acid, which favours aerial oxidation of HI, may thus be avoided. Other ions, *e.g.*, Fe$^{\cdot\cdot}$, Fe$^{\cdot\cdot\cdot}$ and vanadate, also act as catalysts. J. P. STERN

2974. **The analytical control of sodium hydroxide manufacture.** O. Vais (Spolana Ltd., Neratovice, Czechoslovakia). *Chem. Prûmysl*, 1956, **6** (1), 7–9.—Andrews' iodimetric titration of SO_4'' was applied to the estimation of SO_4'' in the presence of a large excess of NaCl. The drawback is the slight solubility of $BaCrO_4$, which can be decreased by addition of $K_2Cr_2O_7$. The error can be eliminated by carrying out a blank with a known content of SO_4''. The determination of Cl, ClO_2' and ClO_3' by using KI is also discussed. To prevent the interference of ClO_3' in determining active chlorine, acetic acid is used in place of mineral acids for acidification. The volumetric determination of ClO_3' can be replaced by a colorimetric method, in which 5 per cent. aniline in 75 per cent. conc. HCl v/v is used. A. O. JAKUBOVIC

2975. **Potentiometric determination of copper with dithio-oxamide.** V. W. Meloche and L. Kalbus (Univ. of Wisconsin, Madison, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1047–1049.—For the potentiometric determination of 1 to 40 p.p.m. of Cu, involving formation of a complex with dithio-oxamide (**I**), a silver indicator electrode gives excellent results in the titration with **I** ($\simeq$ 0·0014 *M*). The end-point is where the max. rate of change of e.m.f. occurs and can be determined to within 0·01 ml. A suitable buffer (pH 4·6) is K H phthalate and NaF in a ratio of 1 and 0·5 per cent. w/v, respectively. The reference curve for Cu concn. *vs.* vol. of **I** is linear. The error is within $\pm$ 1·5 per cent. Concn. of 1000 p.p.m. of Fe, and 400 p.p.m. of Co or Ni do not interfere. Provided that a glass reference-electrode is used, the method is applicable to the titration of $Ag^{\cdot}$ and Hg$^{\cdot\cdot}$ in concn. of 1 to 50 p.p.m. W. J. BAKER

2976. **The reactivity of benzidinesulphonic acids and their applications in analysis. Reaction of cupric salts with o-benzidinemonosulphonic [benzidene-3-sulphonic] acid in presence of alkali thiocyanate.** F. Buscaróns and F. Nieto (Barcelona Univ., Spain). *Anal. Chim. Acta*, 1956, **14** (5), 401–404.—When two drops of a soln. of Cu$^{\cdot\cdot}$ are mixed on a drop plate with three drops of *N* KSCN and one drop of a 1·5 per cent. soln. of benzidine-3-sulphonic acid (neutralised with aq. NH_3), a blue ppt. (when the Cu$^{\cdot\cdot}$ concn. is $\not<$ 1 in 10^5) or a blue colour (when the Cu$^{\cdot\cdot}$ concn. is $\not<$ 1 in $10^{5\cdot7}$) is obtained. The Cu$^{\cdot\cdot}$ soln. must be sufficiently dilute to avoid pptn. of $Cu(SCN)_2$. The Cu, N and S contents of the ppt. have been determined and the possible mechanism of the reaction is discussed. Benzidine-2:2′- and benzidine-3:3′-disulphonic acids do not give the reaction. W. C. JOHNSON

2977. **Spectrophotometric determination of traces of silver co-precipitated with ferrous hydroxide.** H. Triché and G. Rocques (Lab. de Chim. Anal. et Spectrographie, 17 rue Ste-Catherine, Toulouse). *Bull. Soc. Chim. France*, 1955, (11–12), 1507–1509.—It is shown that traces of Ag are completely pptd. with $Fe(OH)_2$ and may be determined spectrographically. *Procedure*—Mohr's salt (100 mg per ml) is added to the solution containing Ag and three drops of conc. aq. NH_3 are added to bring the pH to between 8 and 8·5. The green to black ppt. (interpreted as an aggregate of oppositely charged colloids) is filtered off, and the arc spectrum is photographed; graphite electrodes and an a.c. arc in a high-dispersion instrument (Hilger) are used. For the calibration curve the ratio of intensities of the Ag line at 3382·89 A and the Fe line at 3392·65 A or 3399·33 A is used. The precision is $\simeq \pm 5$ per cent. for 10^{-3} *N* Ag. The effect of other metals (Sb in particular interferes with the 3382·89-A line for Ag) is described. A detailed procedure for application to the determination of Ag in a brass is given. E. J. H. BIRCH

2978. **Differential spectrophotometric determination of beryllium.** J. C. White, A. S. Meyer, jun., and D. L. Manning (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 956–959.—The procedure described is based on measurement of the extinction of the complex of Be with *p*-nitrophenylazo-orcinol in alkaline solution against a reference standard containing 1 mg of Be per 100 ml. Optimum alkalinity is obtained with a sodium borate - sodium citrate buffer (pH 12·7 $\pm$ 0·1), the colour is developed for $<$ 10 min., and the extinctions are measured at 510 mμ in 1-cm cells with a wider than normal slit-width. The error is within 1 per cent.; for max. accuracy the standard curve should be re-established for each analysis. A fivefold excess of either U or Al can be tolerated without causing an error $>$ 2 per cent., whilst F′, even in a 100-fold excess, do not interfere. The method is limited to milligram amounts of Be. W. J. BAKER

2979. **Improvements in the colorimetric magnesium and ammonium methods with sodium polyacrylate.** A. Mehlich (N.C. Agric. Exp. Sta., Raleigh, N.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 518–523.—Sodium polyacrylate is superior to any of the stabilising agents previously used in the determination of Mg by means of thiazole yellow, and of $NH_4^{\cdot}$ by means of Nessler reagent. For the determination of Mg in soils and plants, a compensating solution containing $CaCl_2$, $AlCl_3$, hydroxylamine hydrochloride and triethanolamine is employed to avoid interference by Ca, Al, Mn and Fe. A. A. ELDRIDGE

2980. **Rapid determination of a mixture of dolomite and its components. Theoretical and experimental study.** M. Gibaud and M. Geloso

(Faculté des Sciences, Paris). *Peint-Pigm.-Vern.*, 1956, **32** (4), 306–308.—A comparative thermal analysis of $Mg(OH)_2$, $Ca(OH)_2$, $MgCO_3$, $CaCO_3$ and $MgCa(CO_3)_2$ (dolomite) in air or CO_2 has been carried out with a thermobalance. The method is suitable for identification and determination of dolomite and its constituents, with the exception that $MgCO_3$ cannot be determined simultaneously with the hydroxides. The matter is discussed theoretically. The weight of the sample taken is 1 g, the heating rate is 5° C per min., the gas flow rate is 30 litres per hr. The loss of weight is plotted against temp. Dissociations (in air) show at 380° C [$Mg(OH)_2$], 490° C [$Ca(OH)_2$], 420° C ($MgCO_3$), 790° C ($CaCO_3$) and 800° C (dolomite); and in CO_2,, at 460° and 560° C ($MgCO_3$), 950° C ($CaCO_3$) and 790° and 950° C (dolomite). R. J. COLE

2981. **Analysis of alkaline earths. I. Exchange precipitation.** H. Ballczo and G. Doppler (Second Chem. Lab., Univ. Vienna). *Z. anal. Chem.*, 1956, **151** (1), 16–28.—Consideration of the solubility products of salts (CO_3'', SO_4'', CrO_4'' and oxalates) of Ca, Sr and Ba suggests a method for their quant. separation by anion-exchange precipitation. The cations are first pptd. as oxalates, and Ba is separated by conversion into $BaSO_4$, which remains insol. after ignition. Renewed pptn. of Ca and Sr by K oxalate and K_2CO_3 affords Ca oxalate and $SrCO_3$. For quant. analysis, Ba is determined gravimetrically as $BaSO_4$, and Sr and Ca are determined indirectly by titration of the amount of oxalate consumed. J. P. STERN

2982. **New indicator for titration of calcium with (ethylenedinitrilo)tetra-acetate.** J. Patton and W. Reeder (Campbell Taggart Res. Corp., Dallas, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1026–1028.—In the titration of Ca in the presence of Mg with EDTA (disodium salt), a sharp, stable colour change from wine-red to pure blue is obtained at pH 12 to 14 with 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid as indicator. A procedure, with this indicator, for the accurate determination of Ca and Mg (with no prior separation) in H_2O, salt, limestone and scale is described; it is also valid for samples of blood serum, milk and urine. Interference by small amounts of Ba, Pb, Zn, Co, Ni, Fe and PO_4''' can be controlled, but Sr is reported as Ca. The indicator is prepared (as described) by coupling diazotised 1-amino-2-naphthol-4-sulphonic acid with 2-hydroxy-3-naphthoic acid; it is available commercially. W. J. BAKER

2983. **Chemical analysis of alkaline-earth metals. I. Determination of calcium as molybdate.** Tomoyuki Akiyama, Kenjiro Fujii and Mitsuo Fujiwara (Kyoto Coll. Pharm., Yamashina-Goryo, Higashiyama-ku, Kyoto). *J. Pharm. Soc. Japan*, 1955, **75** (5), 563–566.—A stoicheiometric ppt. of $CaMoO_4$ is quant. obtained with commercial ammonium molybdate at pH 5·8 to 9·2; Ba gives a similar ppt. under the given conditions. The pptd. $CaMoO_4$ can be gravimetrically determined or dissolved in 1·5 *N* HCl and treated with liquid zinc amalgam to reduce Mo^{VI} to Mo^{III}; the $Mo^{\cdots}$ are titrated with 0·1 *N* $KMnO_4$. A significant error results from the presence of $(NH_4)SO_4$ and NH_4NO_3. K. SAITO

2984. **A rapid precise determination of calcium carbonate in small quantities of [deep sea] sediment.** F. Koczky and H. Titze (Oceanographic Inst., Göteborg, Sweden). *Z. anal. Chem.*, 1956, **150** (2), 100–110.—The method of Gripenberg has been modified. Under the conditions of test the error due to ion exchange by the clay in the sediment is negligible. An accuracy within ± 2 per cent. is claimed. To 10 to 100 mg of very finely ground sample add acetic acid (0·2 *N*) (15 ml), barium acetate solution (2 *N*) (5 ml), and pass CO_2-free air through the suspension for 10 min. at a rate of five bubbles per second. Add further barium acetate solution (10 ml), continue bubbling air through and after 5 min. titrate with 0·1 *N* $Ba(OH)_2$ solution (containing 127·7 g of anhydrous barium acetate per litre) to a pH between 7 and 8. From the pH reached and the volume of $Ba(OH)_2$ solution used, calculate the content of $CaCO_3$ from a calibration curve. It is not necessary to titrate to a definite pH. The solution after titration must remain perfectly clear for 20 min. or the determination must be repeated, with longer degassing periods. P. S. STROSS

2985. **Separation of Ra-D, Ra-E and Ra-F by ion exchange.** Tatsujiro Ishimori (Dept. of Chem., St. Paul's Univ., Tokyo). *Bull. Chem. Soc. Japan*, 1955, **28** (6), 432–435.—Carrier-free Ra-D, Ra-E and Ra-F may be separated from each other by ion exchange, the radioactive purity of each fraction being nearly 99·9 per cent. One drop of an HNO_3 (14 *N*) solution of the mixture was added to a column (about 3·0 cm × 0·9 cm in diam.) of Amberlite XE-98 (IR-411) (65 to 120 mesh) and the column was eluted in turn with HCl (2 to 3 *N*) for Ra-D, conc. HCl for Ra-E, and HNO_3 (1:1) for Ra-F. The radioactive substances were co-precipitated with $Fe(OH)_3$; the activity of the Ra-D and Ra-E was measured with a Geiger-Müller counter, end-window type (thickness of window 1·8 mg per sq. cm), and that of Ra-F with a Lauritsen electroscope. The strong acidities of the eluents prevented the formation of radio-colloids. E. G. CUMMINS

2986. **Volumetric method for the simultaneous determination of cadmium and chloride.** J. L. Barton, H. Bloom and N. E. Richards (Auckland Univ. Coll., New Zealand). *Analyst*, 1956, **81**, 245–246.—The method was devised for the determination of Cd and Cl′ in mixtures of $CdCl_2$ and alkali-metal chlorides. The mixture is dissolved in water to make an 0·5 to 1 per cent. soln., a 25-ml aliquot is neutralised to methyl red with 0·05 *N* NaOH, and the Cl′ are determined with 0·1 *N* $AgNO_3$, with dichlorofluorescein as indicator. To precipitate $Cd(OH)_2$ quant., the soln. is heated to above 70° C to coagulate the AgCl, ethanolic thymolphthalein is added, and the liquid is titrated slowly with 0·1 *N* NaOH. The results obtained agree well with those obtained by an electrolytic method. A. O. JONES

2987. **Determination of cadmium in spelter and in Wood's alloy.** W. D. Nordling (Grinnell Corp., Providence, R.I., U.S.A.). *Chemist Analyst*, 1956, **45** (2), 44–45.—The Walter and Freiser method (*cf. Anal. Chem.*, 1952, **24**, 984) is modified by substituting an equal amount of citrate for the tartrate used. The main reagent is 2-*o*-hydroxyphenylbenzoxazole. O. M. WHITTON

2988. **Salicylhydroxamic acid as an analytical reagent. I. Gravimetric estimation of cadmium, uranium and vanadium.** Ajit Sankar Bhaduri (Dept. Applied Chem., Univ. Coll. Sci. Tech.,

Calcutta, India). *Z. anal. Chem.*, 1956, **151** (2), 109–118.—The reactions of 15 metal ions with salicylaldoxime, salicylhydroxamic acid (**I**) and salicylamidoxime are tabulated. The use of **I** for the gravimetric determination of Cd and U, and for the determination of V in the presence of most other elements (except Fe, U and Ti), is described. *Procedure*—For Cd, heat the acid soln. (150 ml, containing $\simeq$ 0·1 g of Cd) to boiling point and add a freshly prepared 0·5 per cent. aq. soln. of **I** in slight excess. Add aq. NH_3 dropwise until the soln. is faintly alkaline, allow the ppt. to settle, cool to room temp. and filter through asbestos. Wash the ppt. with cold water, dry at 110° C and weigh as $Cd(C_7H_5O_3N)$. For U, add a fresh 0·5 per cent. aq. soln. of **I** (50 ml) to the acid soln. (100 ml, containing $\simeq$ 0·05 g of U). Adjust to a pH of 4·4 to 5·4 with aq. NaOH and heat on a water bath until the ppt. settles. Cool to 10° C for 2 to 3 hr., filter through asbestos, wash with cold water and with ethanol, dry at 110° C and weigh as $UO_2(C_7H_6O_3N)_2.2H_2O$. For V, make the soln. (25 ml, containing $<$ 5 mg of V) slightly alkaline, add **I** (0·1 g), ethyl acetate (10 ml) and dil. HCl until acid. Shake vigorously and allow to separate. Evaporate the upper layer to dryness, ignite the residue in air and weigh as V_2O_5. A. R. ROGERS

2989. **A precise, direct, heterometric micro-determination of mercury with diethyldithiocarbamate in excesses of metals. Ethylenediaminetetra-acetate solutions.** M. Bobtelsky and R. Rafailoff (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (4), 339–343.—The method is based on that previously described (*cf. Anal. Abstr.*, 1956, **3**, 2018). An aq. solution (20 ml) containing 0·3 to 1·2 mg of Hg^{II} in the presence of bivalent metals, Fe^{III}, Bi or Th is analysed directly by heterometric titration with 0·0028 *M* Na diethyldithiocarbamate in the presence of excess of EDTA and ammonia. The error is $\pm$ 2·2 per cent. C. A. SLATER

2990. **Improved techniques for the isotopic determination of boron on the mass spectrometer.** C. E. Melton, L. O. Gilpatrick, R. Baldock and R. M. Healy (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1049–1051.—Consecutive mass-spectrometric determinations of small samples of enriched boron isotopes, with BF_3 as carrier gas, are liable to interference by residual adsorbed BF_3, or other compounds, from previous samples. A new method of reducing this "memory" consists in flushing the sample reservoir twice with 0·2 cu. cm of BCl_3 at s.t.p. so as to desorb BF_3, mainly from the glass. The gas for flushing should have an isotopic composition near that of the samples to be analysed. After the sample reservoir is evacuated, it is flushed three times with 0·2 cu. cm of BF_3 (at s.t.p.) from the sample, data being taken only after the fourth flushing. W. J. BAKER

2991. **Titrimetric determination of boric acid. II.** E. Schulek, O. Szakács and M. Szakács (Eötvös Univ., Budapest). *Z. anal. Chem.*, 1956, **151** (1), 1–15.—A method for the separation and micro-determination of H_3BO_3 in minerals, glass, enamel, etc., is described. The H_3BO_3 is separated from metal halides (including fluorides) and nitrates by distillation as methyl borate from 100 per cent. w/v $ZnCl_2$ soln. The ester is hydrolysed and the H_3BO_3 is titrated with NaOH in the presence of neutral mannitol and of 1-naphtholphthalein indicator; a layer of pentane excludes interference by CO_2. The accuracy for 0·5 to 2·5 mg of H_3BO_3 is within $\pm$ 2 per cent., but for larger amounts the accuracy diminishes. *Procedure*—Dissolve the mineral salt (containing B equiv. to $\gtrsim$ 2·5 mg of H_3BO_3) in water (5 to 10 ml) and place in a distillation apparatus (illustrated) with 2 per cent. HCl (2 ml) and 100 per cent. w/v $ZnCl_2$ soln. (5 ml). Distil until the b.p. is 120° C. Cool and, after addition of methanol (30 ml), distil further until the b.p. is 110° C; repeat the addition of methanol and distillation a further three times. Collect the distillate in a 250-ml silver dish containing 5 per cent. NaOH (5 ml). Dilute the combined distillates with an equal vol. of water and evaporate to dryness. Fuse the dry residue with KOH (0·5 to 1 g) and dissolve the melt in water. Acidify the solution and boil off CO_2. Neutralise exactly with 0·01 *N* NaOH (1-naphtholphthalein indicator) and cover the soln. with pentane (5 ml). Add neutral mannitol (0·1 g per ml) and titrate with 0·01 *N* NaOH. J. P. STERN

2992. **The aurintricarboxylates of aluminium, iron and chromium. Composition, structure and analytical use. A heterometric study.** M. Bobtelsky and A. Ben-Bassat (Hebrew Univ., Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (4), 344–355.—All three cations give insoluble, well-defined compounds with aluminon, which have molecular ratios of 1:1, 1:2 and 1:3, respectively. The conditions of pH necessary for pptn. have been worked out and the possibility of determining traces of Fe in the presence of excess of Al and Cr is suggested. C. A. SLATER

2993. **Indirect colorimetric determination of thallium.** Tôru Nozaki (Faculty of Eng., Ehime Univ., Niihama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (3), 493–496.—A small amount of Tl (0·03 to 5 mg) is pptd. as $[Co(NH_3)_6]TlCl_6$ in dil. HCl soln. in the presence of $KClO_3$, and the pptd. *luteo* salt is separated for the Co to be colorimetrically determined by the thiocyanate - acetone method (for $>$ 0·3 mg of Tl). For the decomposition of the pptd. stable complex the use of dil. acetic acid containing H_2O_2, followed by pptn. of CoS with Na_2S, appears to be the best. The black sulphide is dissolved in HNO_3 and treated with HCl, NH_4SCN and acetone. Amounts of Co equiv. to $<$ 0·3 mg of Tl can be determined with nitroso-R salt by the usual method. In the presence of Pb, Hg, Bi and a large amount of Cu, Fe or Zn, the sample soln. containing EDTA (pH 4) is passed through a column of the cation-exchange resin Amberlite IR-120 for $Tl^{\cdot}$ alone to be adsorbed on the resin. The column is eluted with 2 *N* HCl and the eluate is treated with $KClO_3$ and $[Co(NH_3)_6]Cl_3$. K. SAITO

2994. **A photometric determination of samarium in cerite earth mixtures.** R. Rasin-Streden, W. Dauschan and O. Zemek (Treibacher Chem. Werke A.-G., Treibach, Kärnten, Germany). *Mikrochim. Acta*, 1956, (1–3), 512–521.—A method is described for the determination of Sm in chloride solutions by measurement in the absorption band having a peak at 4016 A, by means of monochromatic light of the Hg line 4047 A. With this band neither Pr nor Nd interferes and Er or Eu is present in insufficient quantities in cerite earths to interfere. The slightest trace of Fe causes interference and must be removed by ether extraction. *Procedure*—Dissolve 5 g of cerite oxides in HCl and evaporate to near crystallisation. Transfer to a micro beaker

and add 20 drops of 3 per cent. H_2O_2 to oxidise Fe and reduce Ce^{IV}. Evaporate in the presence of platinum mesh and transfer to a separator (vol. of soln. $\geqslant$ 14 ml). Add 6 ml of conc. HCl and 10 ml of 50 per cent. NH_4SCN soln. Remove the Fe completely by extraction with ether. Make up the iron-free soln. to 50 ml; filter to remove suspended ether droplets and measure the extinction in a 5-cm cell with the use of Hg-Cd 405 filter and a mercury lamp. Because of the relatively weak absorption spectrum of Sm the limit of detection is about 1 per cent. of Sm_2O_3 in oxide mixtures. Errors vary from approx. $\pm$ 1 to $\pm$ 2·5 per cent. at high contents of Sm. An apparatus and procedure for recovering the large volumes of Fe-contaminated ether is described. D. F. PHILLIPS

2995. **Methods for detecting and determining carbon monoxide.** R. L. Beatty (U.S. Gov. Printing Office, Washington, D.C., U.S.A.). *Bull. U.S. Bur. Min.*, No. 557, 1955, 34 pp.—The various methods (I_2O_5, pyrogallol - tannic acid, infra-red gas analysers, colorimetric determination of low concn. with palladous chloride - molybdophosphoric acid - acetone reagent, catalytic combustion in air or O on platinised silica gel, oxidation with heated CuO, chemical absorption, slow combustion on a heated platinum filament, the use of blood as a reagent, etc.) for detecting and determining CO in air and other gaseous mixtures, the range of concn. that may be determined, and the accuracy of the determination are outlined and discussed. Curves are given for calculating the percentage of CO from the percentage of blood saturation. (175 references.) J. M. JACOBS

2996. **Study of the homogeneity of samples of charcoal for analysis by activation of the contained mineral matter in the atomic pile.** A. Blanzat, M. Quesson, J.-L. Soulé and G. Thouzeau (Centre d'Études et Recherches des Charbonnages de France). *Bull. Soc. Chim. France*, 1956, (2), 317–320.—In order to investigate the possible sampling error in semi-micro analysis (sample of 20 mg) of charcoal for C and H compared with macro-analysis (samples of 200 mg), and on the assumption that any variation is due to heterogeneity of distribution of mineral content, a preliminary investigation, with a charcoal having 12·2 per cent. of ash, by activation in the atomic pile (Châtillon) showed that the decay curves (γ radiation with a scintillation counter) were parallel and that the mineral content is therefore uniform. In the main experiment, 20 samples of 200 mg and 20 of 20 mg of a charcoal with 4·55 per cent. of ash were irradiated for 322 hr. at a flux of $1{\cdot}77 \times 10^{11}$ neutrons per sq. cm per sec. Eight days after removal from the pile, the times for 100,000 counts for the 200-mg sample and 10,000 counts for the 20-mg sample were measured, and counts per mg per min. were corrected to an arbitrarily chosen zero-time. The sampling error ($P = 0{\cdot}95$) is $\pm$2·38 per cent. for the 200-mg and $\pm$3·40 per cent. for the 20-mg sample based on the weight of ash, and thus 0·11 per cent. and 0·15 per cent., respectively, on the samples. E. J. H. BIRCH

2997. **Ion-exchange preparation of low-silica hydroxide solutions for colorimetric determinations of total silica.** S. Fisher and R. Kunin (Rohm and Haas Co., Philadelphia, Pa., U.S.A.). *Nature*, 1956, **177**, 1125-1126.—Silica-free hydroxide is prepared by passing a potassium salt soln., *e.g.*, *N* KCl or *N* K_2SO_4, through the hydroxide form of a quaternary ammonium-type anion-exchange resin (Amberlite IRA-400). The resin is first treated successively with 4 per cent. $NaHCO_3$ soln. and 4 per cent. NaOH, and then rinsed to a pH of 9·5 with deionised H_2O. One volume of salt solution per volume of resin is treated in each cycle. The columns are regenerated with $NaHCO_3$ and NaOH between cycles. The hydroxide soln. prepared in this way are sufficiently free from silica to be used in the Straub and Grabowski colorimetric method for determining small concn. of total silica (*cf. Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 574). O. M. WHITTON

2998. **Gravimetric determination of tin in copper alloys with the use of Complexone III as masking reagent.** B. Bieber and Z. Večeřa. *Slévárenství*, 1956, **4** (2), 48–50.—The alloy is dissolved in HCl, and Sn is pptd. as $Sn(OH)_4$ with H_2O_2 and aq. NH_3, with a sufficient quantity of Complexone III to prevent adsorption of foreign ions on the ppt. Interference is caused by Sb, Ti, Be and U; other elements can be determined in the filtrate after removal of the EDTA. S.C.I. ABSTR.

2999. **The quantitative determination of microgram amounts of lead.** F. X. Mayer and P. Schweda (Inst. Medizin, Univ., Vienna). *Mikrochim. Acta*, 1956, (1–3), 485–511.—An investigation into the accurate determination of microgram amounts of Pb by dithizone extraction is described. The prior extraction of Bi at pH 2 is recommended and relationships between extinction values and the pH of the extraction soln. are established. Losses of Pb in the alkaline wash soln. are discussed and it is shown that it is theoretically impossible to determine amounts of Pb $< 1{\cdot}5$ μg by the dithizone method. The polarographic determination of Pb offers numerous possibilities for direct and accurate determination, as Pb gives well-defined waves with a wide choice of supporting electrolytes. Simultaneous determination of other elements such as Bi, Zn, Sn and Tl is possible. Methods of concentrating the Pb before polarographing are described. A simple procedure is given for determination of Pb in the presence of Fe^{III} and the possibilities of internal standard calibrations are reviewed. D. F. PHILLIPS

3000. **Spectrochemical trace analysis following concentration by means of internal electrolysis. [Determination of lead in iron.]** W. Seith and W. Gremm (Inst. for Phys. Chem., Univ. Münster, Westphalia). *Mikrochim. Acta*, 1956, (1–3), 339–342.—A method is described for determining Pb in Fe in which the Pb is deposited on cadmium electrodes by means of internal electrolysis. Dissolve 1 g of sample containing up to 0·1 per cent. of Pb in 10 ml of aq. HCl (1 : 1). Filter off any residue, decompose, dissolve and add to the main solution. To 20 ml of the analysis solution add 15 ml of a solution containing NH_4Cl (135 g), Na acetate (250 g), hydroxylamine hydrochloride (7 g) and gelatin (3 g) made up to 500 ml with H_2O. Add 0·5 mg of Sn in solution as internal standard. "Cementation" of Pb + Sn on to pure cadmium rod (5 mm diam. $\times$ 70 mm long and previously etched in HNO_3) takes 3 hr. and is carried out in a glass vessel with CO_2 stirring. Excitation is by means of a Feussner spark, a rotating cadmium electrode and a graphite counter-electrode with 20 sec. exposure. For a lead content of 0·1 to 0·003 per cent. measure Pb 2823·19 - Sn 2873·58; for a lead content of 0·03 to 0·0001 per cent.

measure Pb 2833·07 - Sn 2813·58. Calibration curves are prepared using Seidel densities. Precautions against lead contamination are described. At a lead content of 0·001 per cent. a mean error of ± 9 per cent. is claimed. A single determination takes 5 hr. D. F. PHILLIPS

3001. **The chemical determination of plumbiferous materials.** R. Collee (University of Liège, Belgium). *Anal. Chim. Acta*, 1956, **14** (5), 430–438.—The compounds of Pb that are commonly present in ores and metallurgical products are separated by the action of selective solvents. The sample, ground to 200 mesh, is first leached with a mixture of ricinoleic acid and methanol which dissolves PbO and $PbSiO_3$. The residue is filtered off and is leached with ammonium acetate soln. to dissolve $PbSO_4$. Further successive residues are treated with HCl to dissolve PbO_2, with aq. H_2O_2 and ammonium acetate soln. to dissolve PbS, and with HNO_3 to dissolve Pb. The Pb is determined separately in each extract by conversion into $PbSO_4$. W. C. JOHNSON

3002. **5:6-Benzoquinaldinic acid as an analytical reagent. II. Determination of titanium.** Anil Kumar Majumdar and Siddheswar Banerjee (College of Engineering and Technology, Calcutta, India). *Anal. Chim. Acta*, 1956, **14** (5), 427–429.—5:6-Benzoquinaldinic acid precipitates Ti^{IV} quant. from soln. of pH < 3·0 and affords a gravimetric determination of the metal. *Procedure*—To a soln. (250 ml) containing ≃ 28 mg of TiO_2 in dil. H_2SO_4 add a slight excess of a 1 per cent. alcoholic soln. of the reagent, heat to boiling point and add 2 *N* aq. NH_3 until the pH is > 3·0; keep the soln. hot for 20 to 30 min., filter, wash the ppt. with hot 1 per cent. NH_4NO_3 soln., dry and ignite, and weigh as TiO_2. When alkaline earths, rare earths or Mg are present add 5 g of NH_4Cl and adjust to pH ≃ 4 with the use of methyl orange screened with indigo carmine. When Th, Zr or Fe^{III} is present add to the original soln. 10 g of NH_4Cl, a few ml of 10 per cent. EDTA (disodium salt) soln., a few ml of 10 per cent. $MgSO_4.7H_2O$ soln., sufficient reagent soln. to ppt. the Ti and a few drops of screened methyl orange soln.; dilute to 250 ml, boil, and add 2 *N* aq. NH_3 until the indicator changes to green; treat the ppt. as in the first procedure. The $MgSO_4$ assists in the pptn. by reducing the masking effect of the EDTA on the Ti. The method does not afford a separation of Ti from Al.
W. C. JOHNSON

3003. **Colorimetric determinations without previous extraction. IV. Titanium determination with cupferron.** F. Buscaróns and J. L. Marín Malumbres (Univ. Barcelona, Spain). *Anales Real Soc. Espan. Fis. Quim., B*, 1955, **51**, 121–124.—To 1 part of the very slightly acid sample containing $TiCl_4$ add 1 part of butane-1:3-diol (**I**) and 0·08 to 0·1 part of conc. HCl. Mix and add 6 per cent. aq. cupferron soln. in an amount which, in a previous experiment without **I**, has been shown to ppt. all the Ti. Mix and after 5 min. compare the colour formed with that obtained from a known soln. of Ti treated in the same way. The dilution limit is 1:3,200,000 and the sensitivity 3 μg.
CHEM. ABSTR.

3004. **Determination of trace elements in titanium by neutron activation analysis.** W. A. Brooksbank, jun., G. W. Leddicotte and S. A. Reynolds (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1033–1035.—From 10^{-4} to 100 μg of any other element in Ti metal or its alloys can be determined qual. or quant. by irradiation of the sample (0·1 to 1 g) in a U - graphite reactor (flux ≃ 10^{12} to 10^{14} neutrons per sq. cm per sec.) for various times so as to form specific radio-isotope(s), which can be separated by radiochemical analysis and the half-life measured. General procedures for the determination of W, Cl, V, Ni, Cu, Mn and Si in Ti and its alloys by neutron activation are described, and the results of some assays are reported. The method is very sensitive and is free of contamination difficulties; the limits of measurement are listed. W. J. BAKER

3005. **Simultaneous determination of carbon and hydrogen in titanium and titanium alloys.** R. B. Nunemaker and S. A. Shrader (Dow Chem. Co., Midland, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1040–1042.—A micro-combustion apparatus and procedure for the determination of from 0·005 to 1 per cent. of C and 0·001 to 0·5 per cent. of H in Ti and its alloys are described. The sample (≃ 0·5 g) is burned, with Fe - Cu - Sn (≃ 0·8 g) as flux, at 1200° C in an alundum-lined boat in a stream of pure O. The CO_2 and H_2O formed are absorbed in Ascarite and $Mg(ClO_4)_2$, respectively. The error is ± 0·005 per cent. for C and ± 0·001 per cent. for H; two analyses can be made in one day. W. J. BAKER

3006. **Separation of zirconium from other elements by liquid - liquid extraction.** F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 997–1001.—Procedures and data are given for the extraction of micro (≡ 10^5 to 10^6 gamma c.p.m.) and macro (1 to 4 mg) amounts of ^{95}Zr from aq. 2 *M* HNO_3 for ≃ 10 min. into an equal vol. of 0·5 *M* thenoyltrifluoroacetone in xylene (**I**) to form a very stable Zr complex. The extraction can also be made, rather less effectively, from 2 *M* HCl, or 0·5 per cent. oxalic acid - 2 *M* HNO_3, as aq. phase. Recovery of Zr is 98 to 99 per cent., and the method can be used to separate ^{95}Zr from other fission products, or Zr from Al, Fe, Th, U or rare earths in analysis. For macro amounts of Zr, the acid concn. should be increased to ≃ 6 *M*. Complete separation of ^{95}Nb and ^{233}Pa from ^{95}Zr can be made by the addition of 1 per cent. H_2O_2 (or 0·5 to 1 *M* $NH_4OH.HCl$) to the acid soln. before extraction with **I**. The extraction must be limited to 10 min. to prevent extraction of ^{59}Fe or Fe^{+++} carrier (≃ 2 mg per ml). General applications of this technique are discussed, *viz*, purification, removal or rapid determination of ^{95}Zr in radio-isotope or fission-product solutions.
W. J. BAKER

3007. **The determination of zirconium in fluoride-containing solutions.** G. W. C. Milner and G. A. Barnett (A.E.R.E., Harwell, England). *Anal. Chim. Acta*, 1956, **14** (5), 414–422.—A method has been devised for the determination of Zr in U - Ti - Zr, U - Nb - Zr and U - Mo - Zr alloys. *Procedure*—Dissolve 1 g of the alloy in 20 ml of dil. HNO_3 (1 + 1) and a few drops of conc. HF and evaporate to 2 ml, fuming with a little conc. $HClO_4$ if necessary to obtain a clear soln. Transfer to a plastic centrifuge tube, diluting to 20 ml, add 10 ml of 5 per cent. aq. $Ba(NO_3)_2$ and 2 ml of conc. HF, set aside for 5 to 10 min., and centrifuge. Add two drops of conc. HF to test for complete pptn. of Zr as barium fluorozirconate. Remove the supernatant liquid by suction through a polyethylene tube, the

end of which is covered with a filter-paper. Wash the ppt. in the centrifuge tube with 10 ml of a filtered soln. containing 1 per cent. w/v of $Ba(NO_3)_2$, 2 per cent. v/v of conc. HF and 10 per cent. v/v of conc. HNO_3, and saturated with barium fluorozirconate by adding a few mg of $Zr(NO_3)_4$ in soln. Dissolve the ppt. in 2 to 3 ml of saturated aq. H_3BO_3 and 10 ml of hot dil. HNO_3 (20 per cent. v/v). Reprecipitate, wash and redissolve as before. Dilute to 30 ml, add an excess of aq. NH_3, centrifuge and wash the $Zr(OH)_4$ with 10 to 15 ml of hot 2 per cent. NH_4Cl soln. Dissolve the ppt. in 10 ml of hot dil. HCl (1 + 1), add 20 ml of $HClO_4$ (60 per cent.) and heat until strong fumes of $HClO_4$ are evolved for 5 to 10 min. Cool, wash down the walls of the vessel with water and evaporate to a vol. of 2 to 3 ml. Dilute with 25 to 50 ml of water and add a slight excess of 0·1 *M* EDTA (disodium salt). Dilute to 300 ml, adjust to pH 2·3, add 1 ml of 2 per cent. K benzohydroxamate soln. and titrate the excess of EDTA with 0·1 *M* $FeCl_3$. Re-adjust the pH to 2·3 as necessary during the titration and take extinction measurements with an EEL photo-electric absorptiometer and an Ilford 605 filter. Plot extinction against vol. of 0·1 *M* $FeCl_3$. The end-point corresponds with the intersection of the two straight-line portions of the graph. When Ta or Nb is present, 1 to 2 drops of aq. H_2O_2 (100 vol.) may be necessary to effect complete solution of the barium fluorozirconate. A high content of W may necessitate the removal of traces of WO_3 from the final soln. No interference results from the presence of Pb, Cu and Fe, but Al and Bi must be absent. When Sn is present the barium fluorozirconate is pptd. from dil. HCl soln. W. C. JOHNSON

3008. **Quantitative spectrographic determination of zirconium and niobium in uranium metal.** J. A. Goleb (Argonne Nat. Lab., Lemont, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 965–967.—A rapid spectrographic method for determining ≃ 5·5 per cent. of Zr and ≃ 1·5 per cent. of Nb in a large number of samples of U metal is described. Excitation is effected by a high-voltage condensed spark, measurements being made on the lines Zr 3214·19 A, Nb 3225·48 A and U 3224·26 A because they are free from interferences, have max. intensity and identical backgrounds. The concn. of Zr and Nb are obtained by comparing the intensity ratios with analytical curves (linear) prepared from homogeneous uranium alloy ingots produced, as described, for spectrographic standards. The reproducibility is within ± 3·0 per cent., whilst the results are within ± 3 per cent. (for Zr) and ±3·95 per cent. (for Nb) of those obtained by the usual chemical method. Since ≃ 25 samples can be analysed daily in triplicate, the method is suitable for detecting segregation (which can vary by 25 per cent.) along an 8-in. bar.

W. J. BAKER

3009. **5:6-Benzoquinaldinic acid as an analytical reagent. I. Determination of thorium and zirconium.** A. K. Majumdar and S. Banerjee (Coll. of Eng. and Technol., Calcutta, India). *Anal. Chim. Acta*, 1956, **14** (4), 306–310.—Thorium and zirconium may be determined in the presence of rare earths, alkaline earths and magnesium by pptn. with 5:6-benzoquinaldinic acid (**I**). Thorium is completely pptd. at pH 3·0 as $Th(C_{14}H_8O_2N)_4$. Zirconium is pptd. at pH 1·8, but since the composition of the ppt. is not stoicheiometric it is necessary to ignite to the oxide before weighing. *Procedure*—Soln. containing Th or Zr are adjusted to the desired pH after diluting to about 200 ml and heated to boiling point. To the hot soln. is added **I** in 1 per cent. ethanolic soln. until pptn. is complete. The soln. is kept hot for 15 min., then filtered, and the filtrate is washed with hot 1 per cent. NH_4NO_3 solution. The ppt. of the Th compound is collected in a Gooch crucible and further washed with hot water, ethanol and acetone, dried at 110° C and weighed. For Zr, the ppt. at pH 1·8 is ignited to the oxide and weighed.

C. A. SLATER

3010. **Spectrophotometric estimation of thorium by morellin.** B. R. L. Rao and C. C. Patel (Indian Inst. Sci., Bangalore). *Proc. Indian Acad. Sci., A*, 1955, **42** (6), 317–325.—The determination described is based on the formation of a 4:1 morellin - Th complex in alcoholic soln., which is stable at pH 5 to 7. *Procedure*—An ethanolic $1{\cdot}352 \times 10^{-3}$ *M* soln. (1·5 ml) of morellin (*cf.* Rao *et al.*, *Naturwissenschaften*, 1954, **41**, 66) (mol. wt. = 544) is made up to 10 ml with 50 per cent. ethanol and mixed with 0·3 ml of Th soln. of ≃ equimolecular concn. and the extinction is determined at 515 mμ. The results are compared with a standard curve made from a soln. having a morellin to Th mol. ratio of 5; Beer's law is obeyed at all concn. between 1·4 and 25 p.p.m. of Th. The limiting concn. of 30 interfering salts are tabulated. Trace quantities of the oxalates, iodates, phosphates, fluorides and carbonates of Na, K and ammonium also interfere.

G. R. WHALLEY

3011. **Determination of micro amounts of thorium. III. Colorimetric estimation of a micro amount of thorium in rocks and sediments.** Masayoshi Ishibashi and Shinnosuke Higashi (Dept. of Chem., Faculty of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1956, **5** (3), 135–138.—The authors' colorimetric determination of Th with "neo-thorin" (*o*-arsonophenylazochromotropic acid) (**I**) (*cf. Anal. Abstr.*, 1955, **2**, 2387) was applied to the analysis of Th (1 to 15 μg per g) in rocks and sediments. The sample (1 to 3 g) is decomposed with HNO_3, $HClO_4$ and HF, and fused with $KHSO_4$. The cake is dissolved in HCl (1 + 10) (25 ml), treated with aq. NH_3 soln. and the ppt. is dissolved in HCl to be repptd. at pH 5·5 in the presence of hydroxylamine hydrochloride. The Th, co-pptd. with $Al(OH)_3$, is dissolved in a small amount of HNO_3, treated with $Al(NO_3)_3$ (1 g; masking agent for F' and PO_4''') and NH_4NO_3 (10 g) (total vol. 10 to 12 ml, pH 0·65) and extracted with *cyclo*hexanone (3 × 10 ml). Thorium is then transferred to an aq. soln. by shaking the *cyclo*hexanone soln. with water; the aq. soln. is treated with **I** (0·1 per cent., 0·5 ml per 10 ml) at pH 1·0 in the presence of ascorbic acid (to reduce the last trace of Fe'''), and submitted to colorimetry at 600 mμ.

K. SAITO

3012. **Titrimetric determination of hydrazine with alkaline permanganate.** I. M. Issa and R. M. Issa (Cairo Univ., Giza, Egypt). *Chemist Analyst*, 1956, **45** (2), 40–41.—The sample hydrazine soln. is adjusted so that it is about 0·05 *N*. The $KMnO_4$ soln. (0·1 *N*) (25 ml) is mixed with telluric acid (0·2 g) (which dissolves pptd. manganese dioxide and thus prevents catalytic decomposition of permanganate) and enough 5 *N* NaOH soln. to make the final mixture with sample soln. 0·1 to 1·0 *N* in alkali. After adding from 3 to 10 ml of the hydrazine soln. and mixing well, the mixture is allowed to stand for 3 to 5 min. and then poured

into an ice-cold soln. of standard $Fe(NH_4)_2(SO_4)_2$ soln. made 4 *N* in H_2SO_4. Phosphoric acid is added and the excess of Fe^{++} is titrated with standard 0·1 *N* $KMnO_4$. Typical results are given. They indicate that 0·01 *N* $KMnO_4$ can also be used. O. M. WHITTON

3013. **Chelatometric determination of phosphoric acid precipitated by aminoethanol [ethanolamine] after separation of iron and aluminium with cupferron.** H. Eschmann and R. Brochon (Cantonal Lab., Berne, Switzerland). *Chemist Analyst*, 1956, **45** (2), 38–39.—The sample soln., about 0·5 *M* in HCl, is evaporated to small bulk to effect rapid conversion of any pyrophosphoric acid into orthophosphoric acid. Iron and Al are extracted with cupferron soln., and Co, Cu and Ni are complexed with a predetermined amount of EDTA. The orthophosphate is then pptd. with aq. 2-aminoethanol at pH 9 as magnesium ammonium phosphate hexahydrate, which is separated, dissolved in HCl, and titrated with EDTA, with Eriochrome black T as indicator. O. M. WHITTON

3014. **Photometric determination of phosphoric acid and silicic acid in solution, involving extraction with *iso*butyl alcohol.** E. Ruf (T. Goldschmidt A.-G., Essen, Germany). *Z. anal. Chem.*, 1956, **151** (3), 169–184.—Small amounts of phosphoric acid and silicic acid can be quant. determined by means of the blue colours formed on reduction of their complexes with molybdic acid. Separation is based on the fact that molybdophosphoric acid, but not molybdosilicic acid, is extracted by *iso*butyl alcohol from an aq. soln. of pH 1·5 or 2. Recoveries in five experiments ranged from 98 to 103·3 per cent. *Procedure*—Neutralise the sample (containing < 280 μg each of P and Si) to phenolphthalein, mix with ammonium molybdate soln. (0·6 *M* in Mo) (1·5 ml) and 2 *N* HCl (0·6 ml), and dilute to 50 ml with H_2O. Extract twice with *iso*butyl alcohol (30 ml and 20 ml) and wash the combined extracts with 0·01 *N* HCl (30 ml). Reserve the *iso*butyl alcohol soln. (*A*) for the determination of P. *For silicic acid*—Mix the aq. soln. and washings with ammonium molybdate soln. (0·5 ml) and 2 *N* HCl (0·25 ml) and dilute to 100 ml with H_2O. After 35 min., add conc. HCl (10 ml) and extract twice with *iso*butyl alcohol (30 ml and 25 ml). Wash the combined extracts with 1·5 *N* HCl (30 ml) and reject the washings. Add H_2O (30 ml) and $CHCl_3$ (25 ml) and shake. Wash the lower layer with H_2O (25 ml). Mix the upper aq. layer and the washings with conc. HCl (10 ml) and H_2O (50 ml) and reduce with freshly prepared $SnCl_2$ soln. (0·1 *M* in Sn, 2 *N* in HCl) (2 ml). Dilute to 200 ml with H_2O and measure the extinction at 730 mμ; calculate the silicic acid concn. by the use of a standard curve. *For P*—Extract the *iso*butyl alcohol soln. (*A*) first with a soln. of metol (8 mg), Na_2SO_3 (40 mg) and $NaHSO_3$ (1·2 g) in H_2O (30 ml), then with H_2O (30 ml). Dilute the aq. extracts to 100 ml with H_2O and measure the extinction at 730 mμ; calculate the phosphoric acid concn. by use of a standard curve. A. R. ROGERS

3015. **Oxidations with alkaline permanganate using univalent thallium for the back-titration. III. Estimation of tervalent arsenic.** I. M. Issa and I. M. El Sherif (Cairo Univ., Egypt). *Anal. Chim. Acta*, 1956, **14** (4), 300–305.—In the absence of Ba^{++}, permanganate is reduced by arsenite directly to MnO_2. The reduction can be checked at the manganate stage in the presence of *N* NaOH and Ba^{++} equal to three times that equivalent to MnO_4'' and arsenate. In the absence of Ba^{++} the end-points are attained later than the MnO_2 stage. As^{III} can be estimated by mixing with excess of permanganate in the presence of Ba^{++} in *N* NaOH soln., or in 1·5 to 3 *N* NaOH in their absence. Excess of oxidant is back-titrated with thallium. C. A. SLATER

3016. **Notes on cerimetric analysis. III. The cerimetric micro-determination of antimony by the method of Rathsburg.** A. Petzold (Inst. of Mining, Freiberg, Saxony, Germany). *Z. anal. Chem.*, 1956, **150** (2), 111–114.—The determination of small quantities of Sb in forensic samples containing tartaric acid (*cf.* Furman, *J. Amer. Chem. Soc.*, 1932, **54**, 4235) necessitates the accurate control of the concn. of HCl when 0·01 *N* ceric sulphate solution is used for the titration. In the presence of 3 per cent. tartaric acid, accurate results are obtained only in the presence of 20 to 25 per cent. v/v of conc. HCl, whereas in the absence of tartaric acid, 17 to 22 per cent. v/v of conc. HCl should be used. Methyl red was found to be a better indicator than methyl orange, and a blank determination is necessary. P. S. STROSS

3017. **A new selective and sensitive method of bismuth determination.** M. Oosting (Inst. Anal. Chem. T.N.O. Rijswijk, Holland). *Mikrochim. Acta*, 1956, (1–3), 528–534.—Bismuth is determined by extracting the brucine - bismuth iodide complex with chloroform and measuring the light absorption at 425 mμ. The presence of other elements causes relatively slight interference, but Bi can be isolated if necessary by extracting with Na diethyldithiocarbamate at pH 11 to 12 in the presence of KCN and of EDTA. *Procedure (without isolation of Bi)*—Place 50 to 100 ml of soln. containing 10 to 400 μg of Bi in 1 to 2 *N* H_2SO_4 in a separating funnel. Add 2 ml of SO_2 soln., 3 ml of 10 per cent. KI soln. and 5 ml of 1 per cent. brucine in 25 per cent. citric acid soln. Mix, and extract with 5-ml portions of $CHCl_3$ which, after filtering through glass wool, are run into a dry 25-ml measuring flask. Extraction of Bi is generally complete after two extractions. Make up to 25 ml with $CHCl_3$ and measure the extinction against a blank at 425 mμ in a Coleman spectrophotometer or with filter 45 in an Engel colorimeter. Details are given for preliminary separation of Bi from all other elements. D. F. PHILLIPS

3018. **Controlled potential electrolysis. X. Determination of bismuth in the presence of a large amount of silver.** Masayoshi Ishibashi, Taitiro Fujinaga and Masanori Sato (Chem. Dept., Faculty of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *Japan Analyst*, 1956, **5** (2), 77–79.—A small amount of Bi in Ag (> 0·004 per cent.) is separated by controlled potential electrolysis (1 hr.) at −0·20 V *vs.* a mercury sulphate electrode (+ 0·23 V *vs.* the S.C.E.) in 2 *N* HNO_3 soln. and polarographically or photometrically determined. To prevent the deposition of Ag_2O_2 on the anode, the addition of ethanol (5 ml for 50 ml of the electrolytic soln.) is recommended. A 20-ml portion of the soln. is mixed with a soln. containing *M* ammonium acetate and 0·2 *M* tartaric acid and the wave height of Bi (> 0·2 mg) (−0·2 V *vs.* the S.C.E.) is compared with the standard; Cu ($E_{\frac{1}{2}}$, −0·08 V) (< 10 mg in 50 ml) does not interfere. When the content of Bi

is between 0·02 and 0·2 mg, it is determined in the electrolytic soln. by Sandell's method. K. SAITO

3019. **Compleximetric titrations (chelatometry). XV. Catechol violet as a new specific indicator. Estimation of bismuth (and thorium) in the presence of iron and mercury.** J. Cífka, M. Malát and V. Suk (Inst. Anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (2), 412–417.—Tervalent Fe interferes in the complexim etric estimation of Bi and Th with catechol violet as indicator. Its effect is eliminated by reduction to Fe^{II} with a small excess of freshly prepared ascorbic acid. The addition of formic or ascorbic acid enables Bi to be estimated in the presence of Hg, if the ratio of Hg to Bi is $\not> 10:1$. *Procedure*—The soln. of bismuth and iron nitrates is diluted to between 50 and 100 ml, and is adjusted with dil. aq. NH_3 to a pH of 2·0 to 2·5. After the addition of five drops of sulphosalicylic acid (2 per cent. soln.), freshly prepared ascorbic acid (1 per cent. soln.) is added with stirring until the red colour of the indicator disappears, followed by 1 to 2 ml in excess. A few drops of catechol violet (0·1 aq. soln.) are introduced, and the Bi is titrated complexim etrically until the indicator changes from blue to lemon yellow. Thorium is estimated similarly, but a pH of 2·5 to 3·5 is employed. For the estimation of Bi in the presence of Hg, the nitrate soln. is brought to a pH of 2·0 to 2·5, and 3 ml of ascorbic acid soln. are added, and 1 ml for each further 10 mg of Hg. After $\simeq$ 1 min., the catechol violet indicator is added and the soln. is titrated immediately. If formic acid is used to reduce the Hg, 1·5 ml of a 5 per cent. soln. are added for each 10 mg of Hg (but $\not< 2$ ml). The soln. is boiled for 1 to 2 min. and is titrated after cooling.
J. H. WATON

3020. **Compleximetric titrations (chelatometry). XVI. Estimation of bismuth, nickel and cobalt with pyrogallol red.** V. Suk, M. Malát and A. Jeníčková (Inst. Anal. Chem., Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (2), 418–422.—The use of pyrogallolsulphonephthalein (pyrogallol red) indicator enables Bi to be determined complexim etrically in acid soln. in the presence of Ag, Pb, Cd, Al, Co, Ni, Mn, Zn, Ca, Sr, Ba, Mg, NH_4^+, K and Na. The interference of Fe and Hg is eliminated by the use of ascorbic acid (*cf. Anal. Abstr.*, 1956, **3**, 3019). In weakly alkaline soln., Ni or Co can be determined, provided that there are < 20 mg of Ni or < 5 mg of Co in 100 ml of soln. *Procedure*—The nitric acid soln. of Bi is diluted so that the concn. is $\not> 80$ mg per 100 ml of soln. The pH is adjusted to between 2 and 3 with dil. aq. NH_3, and 15 to 20 drops of indicator (0·05 g of pyrogallol red in 100 ml of 50 per cent. ethanol) are added. The Bi is titrated with EDTA (disodium salt) soln. until the colour changes from red to orange-yellow. For the estimation of Ni and Co, in each case 10 ml of a buffer soln. (equal vol. of *N* NH_4Cl and *N* aq. NH_3) are added, followed by 15 to 20 drops of indicator. Both soln. are titrated complexim etrically until the indicator changes from blue to red. If the concn. of Ni approaches the max. permitted, the end-point is taken as the colour change from blue to violet. J. H. WATON

3021. **Determination of vanadium in iron and steel.** Shigeo Wakamatsu (Toto Seiko Co., Ltd., 5–1985, Minamisuna-machi, Koto-ku, Tokyo). *Japan Analyst*, 1956, **5** (2), 84–87.—A rapid ($<$ 20 min.) determination of V in iron and steel was studied by the use of $HClO_4$ as an oxidising agent and by direct titration with ferrous iron. Chromium is removed as chromyl chloride but results are not satisfactory if the amount of Fe is >100 times that of the Cr. *Procedure*—The sample (1 g) is attacked with $HClO_4$ (60 per cent., 30 to 50 ml) at 200° C and heated to 300° C until white fumes are evolved, then NaCl (0·5 to 3 g, according to the amount of Cr) is added in small portions. The product, free from Cr, is cooled, dissolved in water (15 ml) and H_3PO_4 (sp. gr. 1·7, 20 ml) and titrated with *N*/30 $Fe(NH_4)_2(SO_4)_2$, with diphenylamine (1 per cent. in H_3PO_4, 3 to 4 drops) as indicator. No significant error results from the presence of W ($<$ 20 per cent.). K. SAITO

3022. **The polarography of niobium.** D. J. Ferrett and G. W. C. Milner (A.E.R.E., Harwell, Berks., England). *J. Chem. Soc.*, 1956, 1186–1192.—The polarographic behaviour of Nb in various complexing solutions, with both conventional equipment and a square-wave polarograph, is described. Previous work in sulphuric, hydrochloric, tartaric and oxalic acids has been reinvestigated and the use of EDTA has been studied. Polarographic steps for Nb have been found in malic, lactic, gluconic and citric acids and, of these complexes, niobium citrate is the most stable to hydrolysis and is easily prepared. The step at $-0{\cdot}86$ V (*vs.* the S.C.E.) from 2 *M* citric acid solutions of pH 1 can be used to determine from 0·1 to at least 250 μg of Nb per ml and is well separated from the uranium wave in the same solution. There is interference from Sb, Ti and Mo, but none from Mn, Ni, Cr, Fe and W.
K. A. PROCTOR

3023. **The determination of niobium in some African low-grade minerals and mineral dressing products. II. Spectrographic.** R. P. Thorne and B. M. Childs (A.E.R.E., Harwell, England). A.E.R.E. Publication C/R 1232/2, 1955, 8 pp.—A variation of the "iron flux" method has been applied to the estimation of Nb. One part by wt. of the sample is thoroughly ground with 10 parts by wt. of a flux consisting of equal wt. of titanium oxide and ammonium sulphate. Small pellets, prepared from this mixture, are arced on copper supporting electrodes and the region 3700 to 5000 A is recorded, the glass optics of a Littrow spectrograph being used. The line pair used is Ti 4145·0 - Nb 4100·9, or Ti 4052·9 - Nb 4058·9 if Mn is absent. Working curves are prepared from synthetic standards made by adding Nb_2O_5 to the flux. The accuracy of analysis is ± 10 per cent. over the range 0·05 to 0·5 per cent. of Nb_2O_5. P. T. BEALE

3024. **A modified ethylenediaminetetra-acetic acid - tannic acid procedure for the determination of niobium, tantalum and titanium together in minerals.** M. Sankar Das, C. Venkateswarlu and V. T. Athavale (Atomic Energy Estab., Bombay, India). *Analyst*, 1956, **81**, 239–242.—The mineral (0·25 g) is thoroughly fused with $KHSO_4$, the melt is dissolved in a warm mixture of saturated oxalic acid soln., conc. HCl and water, and filtered, the paper being washed with water containing oxalic acid and HCl. The filtrate is treated with saturated NH_4Cl soln., tartaric acid (0·5 g) and 25 ml of 10 per cent. EDTA (disodium salt) soln., the pH is adjusted to between 5 and 6, and 50 ml of 10 per cent. tannic acid soln. are added to the boiling liquid. The ppt. is collected, washed back into

the original beaker, churned well with a wash liquid containing tannic acid, NH_4Cl and 1 per cent. of EDTA soln., collected on the original paper and washed first with the wash liquid (*supra*) and then with wash liquid not containing EDTA. Finally the ppt. is ignited and weighed as the mixed oxides. Interference is caused by Sb and Sn; Sb can be initially separated by means of H_2S from the oxalate soln.; Sn cannot be removed thus, but is collected with the mixed oxides and is then separated by means of H_2S from a soln. of the fused mixed oxides in tartaric acid soln. and the wt. of the mixed oxides is correspondingly corrected. Tungsten interferes only when present in amounts $>$ 4 per cent. A. O. JONES

3025. **Fluorescent X-ray spectrographic determination of tantalum in commercial niobium oxides.** W. J. Campbell and H. F. Carl (Bur. Mines, U.S. Dept. Interior, College Park, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 960–962.—From 0·5 to 10 per cent. of Ta_2O_5 in crude or refined Nb_2O_5 can be determined to within $\pm$ 5 per cent. by an improved fluorescent X-ray spectrographic procedure that sharply resolves the L_{α_1} line of Ta without much loss of intensity. Line intensities of 750 counts per sec. can be obtained from a sample containing 5 per cent. of Ta_2O_5 with a molybdenum target X-ray tube, a quartz analyser and a slit collimator (4 in. long and 0·005-in. spacing). Both hand-mixed and chemically pptd. samples of Ta_2O_5 (10 to 80 per cent.) in Nb_2O_5 are suitable as standards, but hand-mixed Ta_2O_5 in pure ZrO_2 is preferred when analysing high-purity Nb_2O_5. Below 0·5 per cent. of Ta_2O_5, the error increases continuously as the lower limit (0·03 per cent.) of detection is approached. Except for TiO_2, the usual impurities (SnO_2, FeO, Na_2SO_4) in Nb_2O_5 cause no appreciable error if their concn. are $<$ 1 per cent., but a correction must be made for the effect of TiO_2, especially in crude samples that may contain up to 12 per cent. One analysis can be made in $\simeq$ 10 min. after prep. of standards. W. J. BAKER

3026. **Comments on a modified Tutwiler method for the determination of H_2S and SO_2 in gases.** H. A. C. van Straten (Koninkl. Shell-Lab., Amsterdam). *Anal. Chim. Acta*, 1956, **14** (4), 325–328.—An examination of the modified Tutwiler analysis (Sawyer *et al.*, *Ind. Eng. Chem.*, 1950, **42**, 1938) has shown this to be suitable for the determination of H_2S alone in the Claus sulphur-recovery process. With a small modification the method is also applicable to SO_2 alone. The method is not suitable for both compounds if they occur together and a method recently published is recommended (van Straten and van de Craats, "L'analyse des gaz dans l'industrie de récupération du soufre selon le procédé Claus." *Proc. 27e Congr. Chim. Ind., Brussels*, Sept. 1954, Vol. II, p. 612). C. A. SLATER

3027. **The determination of small amounts of sulphate by reduction to hydrogen sulphide and titration with mercuric or cadmium salts, with dithizone as indicator.** E. E. Archer (The Distillers Co. Ltd., Epsom, Surrey, England). *Analyst*, 1956, **81**, 181–182.—In the method described, H_2S is evolved from sulphates by means of a reduction mixture (prep. described) containing HI, H_3PO_2 and HCl. The soln. containing SO_4'' is treated with the reduction mixture in a 25-ml flask having a side arm through which a stream of N can be passed through the liquid. The flask is heated on a water bath at 100° C and the products of reaction pass through a water reflux-condenser into a specimen tube containing a few micrograms of dithizone with *N* NaOH soln. and acetone (3 ml of each) and a drop of standard mercuric acetate soln. (0·001 *M*). As H_2S is evolved the colour of the contents of the tube changes from red to yellow. Heating is continued for 20 min. and then, with the N still passing, the liquid is titrated with the mercuric acetate soln. until a red colour persists. Cadmium sulphate can be used as titrant, but the accuracy is less with small amounts of SO_4''. Results of the application of the method to the determination of up to 128 μg of S indicate satisfactory accuracy. A. O. JONES

3028. **A conductimetric method for the determination of free acids in the presence of metal salts liable to hydrolyse. I. The determination of free sulphuric acid in the presence of titanium (IV), chromium (III) and iron (III) sulphates.** H. Hahn and F. Burow (Inst. anorg. Chem., Univ. Kiel, Germany). *Z. anal. Chem.*, 1956, **151** (2), 91–98.—The intersection of the lines in a plot of conductance against vol. of alkali added in the conductimetric titration of H_2SO_4 in the presence of $Ti(SO_4)_2$, $Cr_2(SO_4)_3$ or $Fe_2(SO_4)_3$ gives the equivalent of total acid (free acid plus acid due to hydrolysis). The end-point corresponding to free acid alone is obtained by producing the line that represents neutralisation of free acid (and which is distorted near the end-point owing to hydrolysis) to the point of intersection with a line that represents the conductance at the end-point corresponding to total acid. The titration of 42 mixtures of H_2SO_4 (40 to 120 mg) with metal salts ($<$ 200 mg) showed that the maximum deviation of a single determination is $<$ $\pm$ 1 per cent.; the accuracy is independent of the amount of salt present. A. R. ROGERS

3029. **An indirect polarographic method for the determination of micro quantities of selenium.** H. Hahn and W. Kleinwort (Inst. anorg. Chem., Univ. Kiel, Germany). *Z. anal. Chem.*, 1956, **151** (2), 98–104.—Small amounts of Se can be determined by reduction with hydrazine in the presence of excess of $TlNO_3$; TlSe is pptd. and the excess of Tl^I is determined polarographically. The accuracy is dependent on the amount of Se, varying from $\pm$ 1 per cent. (5 mg) to $\pm$ 5 per cent. (20 μg). *Procedure*—Neutralise the solution of the selenite with aq. NH_3 and add an aq. soln. of $TlNO_3$ (three-fold excess). Add NH_4NO_3 and aq. NH_3 (to make the final soln. 0·5 *M* in each). Heat in a covered flask on a bath of boiling water for 5 min. Add two portions of powdered hydrazine sulphate (each in 30-fold excess) and heat for 30 min. after each addition. Dilute to volume. Add gelatin (0·01 per cent.) to an aliquot, deoxygenate with H for 20 min., and record the polarogram from $-$0·2 to $-$0·6 V *vs.* the S.C.E.; $E_{\frac{1}{2}} = -0{\cdot}46$ or $-0{\cdot}47$ V. A. R. ROGERS

3030. **Micro-methods in semi-conductor research. [Determination of trace elements in selenium.]** F. A. Pohl (Allg. Elektricitätsges. A.E.G., Belecke-Möhne, Germany). *Mikrochim. Acta*, 1956, (1–3), 414–421.—Discrepancies in published values for the conductivity of semi-conducting elements may be attributed to the presence of trace impurities in the crystal lattice. Whilst no serious difficulties exist in determining metallic impurities there is little information available on the determination of trace non-metallic elements. A micro-method

for the determination of between 10^{-2} to 10^{-4} per cent. of Cl and Br in Se is described. Dissolve 100 to 500 mg of Se in halogen-free HNO_3 in the presence of a large excess of $AgNO_3$. Reduce the resulting silver halides with hydrazine in NaOH soln. Dissolve the Ag in HNO_3 and in a maximum volume of 0·5 ml titrate with 0·02 *N* KSCN in a Gorbach membrane burette. Determine Br separately as tetrabromofluorescein photometrically in the filtrate from the silver reduction and calculate the chloride content from the two results. It is claimed that from 2 μg upwards of halogen in Se can be determined within ± 5 per cent.

D. F. PHILLIPS

3031. **Paper electrophoresis of seleno- and telluro-thionates.** H. W. Wood (Ilford Res. Lab., Ilford Ltd., Essex, England). *Chem. & Ind.*, 1956, (21), 468–469.—Paper electrophoresis of selenodithionates, selenotetrathionates and tellurotetrathionates was carried out (*cf. J. Photogr. Sci.*, 1954, **2**, 154) and anions were located on the electropherograms by spraying with $AgNO_3$ solution. Mobilities are given, compared with those of some polydithionates, and discussed. O. M. WHITTON

3032. **Amperometric titrations. VI. Use of an oxide electrode of a high positive potential and its application to the determination of chromate and vanadate with ferrous iron.** Masayoshi Ishibashi, Taitiro Fujinaga and Huziko Sinozuka (Dept. of Chem., Faculty of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (2), 265–266.—The amperometric titration of CrO_4'' and VO_3' with $Fe^{\cdot\cdot}$ was studied without application of external potential (Ishibashi *et al.*, *Bull. Chem. Soc. Japan*, 1952, **25**, 142). A rotating platinum electrode is connected through a galvanometer with a cathode of MnO_2 inserted in an aq. soln. containing *N* H_2SO_4 and *M* $MnSO_4$; this soln. is in contact with the sample soln. through a sintered-glass diaphragm. The rotating platinum electrode is inserted in the sample soln. containing *N* H_2SO_4 and the current is plotted against the amount of $Fe^{\cdot\cdot}$. At the end-point the current increases markedly, owing to the oxidation diffusion current of $Fe^{\cdot\cdot}$. The relative error is $\simeq$ 1 per cent. for < 1 mg of Cr and for < 10 mg of V. The potential of the oxide cathode (+ 1·07 V *vs.* the S.C.E.) remains constant throughout the titration.

K. SAITO

3033. **Rapid determination of molybdenum in ferromolybdenum by titration with copper sulphate.** Ken Saito (Dept. of Techno-Anal. Chem., Faculty of Eng., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1956, **5** (3), 153–156.—A rapid (< 40 min.) determination of Mo in ferromolybdenum was studied by a reduction with liquid cadmium amalgam, followed by oxidation titration with $CuSO_4$. When the reduction is carried out in an aq. soln. containing 6 *N* HCl and *N* H_2SO_4, no significant error results from the presence of $Fe^{\cdot\cdot\cdot}$ (< 0·1 g), Ni (< 50 mg), Co (< 50 mg), Cu (< 10 mg), W (< 2 mg), As (< 70 μg), V (< 3 mg) and Cr (< 6 mg). The sample (0·1 to 0·2 g) is dissolved in H_2SO_4 (1 + 1, 10 to 15 ml) and HNO_3 (sp. gr. 1·4, 1 to 2 ml) and heated two or three times to white fumes until HNO_3 is completely removed. The product is transferred to a reductor with HCl and diluted to produce 6 *N* HCl and *N* H_2SO_4 soln. This is shaken with cadmium amalgam (100 to 150 g) and titrated with 0·1 *N* $CuSO_4$; safranine (0·5 per cent., 1 ml) is used as indicator.

K. SAITO

3034. **Colorimetric determination of molybdenum in tungsten metals and compounds.** E. M. Goldstein (Montclair Res. Lab., Montclair, N.J., U.S.A.). *Chemist Analyst*, 1956, **45** (2), 47–49.—The sample, which should contain 0·27 g of tungstic acid, 0·25 g of tungstic oxide or 0·28 g of ammonium paratungstate, is dissolved in 5 ml of solvent (prepared from 40 g of NaOH, 150 g of Na citrate dihydrate in water, 2 ml of chloroform and 60 ml of 91 per cent. *iso*propyl alcohol, diluted to 1 litre with water). Tungsten metal should first be converted into the oxide by ignition. Phenylhydrazine soln. (2 v/v in 8 v/v acetic acid soln., 25 ml) is added, and the mixture is warmed on a water bath for 15 min. (at 80° C) to develop the red colour. The extinction is measured at 420 mμ, against a blank, or the colour may be measured visually against standards. In the presence of much Mo, both sample and blank should be diluted with a mixture of Na citrate, aq. acetic acid and *iso*propyl alcohol. Molybdenum contents as low as 0·05 per cent. can be determined. O. M. WHITTON

3035. **The effect of phosphoric acid on the volumetric determination of uranium. (Metallic reducing agents in analytical chemistry.)** Chozo Yoshimura (Chem. Dept., Faculty of Eng., Kinki Univ., Fuse, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 1–4.—The reduction of U^{VI} with liquid zinc amalgam or with a Jones reductor was studied polarographically in H_3PO_4 soln. Schreyer's result (*Anal. Chem.*, 1953, **25**, 644) that addition of a large amount of H_3PO_4 prevents the production of U^{III} was re-examined and found to be incorrect, although the amount of the U^{III} is decreased. The rate of reduction from U^{VI} to U^{IV} is markedly decreased by H_3PO_4. K. SAITO

3036. **Volumetric estimation of uranium. III. [Titration] with ceric sulphate using diphenylbenzidine and N-phenylanthranilic acid as internal indicators.** V. Panduranga Rao, B. V. S. R. Murty and G. Gopala Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1956, **150** (6), 401–407.—With diphenylamine, diphenylbenzidine, diphenylaminesulphonic acid, or N-phenylanthranilic acid as internal indicator, U^{IV} (10 to 25 mg) is smoothly determined at room temp. by titration with $Ce(SO_4)_2$ in 0·5 to 1·0 *N* H_2SO_4 in the presence of H_3PO_4 (3 to 5 ml of 80 per cent. H_3PO_4 for 50 ml of reaction medium). J. P. STERN

3037. **Titrations of halides with electrolytically generated mercurous ion.** D. D. DeFord and H. Horn (Northwestern Univ., Evanston, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 797–798.—From 0·2 to 4 milli-equiv. of Cl′, Br′ or I′ can be determined accurately and precisely by coulometric titration with $Hg^{\cdot}$ generated at 100 per cent. current efficiency at large mercury-pool anodes. The supporting electrolyte is 0·5 *M* $HClO_4$ for Cl′ and Br′, and 0·4 *M* KNO_3 plus 0·1 *M* $HClO_4$ for I′. Even at the lowest current used (50 mA), the equivalence point can be located to within a few tenths of a sec. The mean errors are approx. ± 0·1 per cent. for Cl′, + 0·07 per cent. for Br′, and + 0·1 to 0·3 per cent. for I′. W. J. BAKER

3038. **Rapid argentimetric determination of halides by direct potentiometric titration.** V. J. Shiner, jun., and M. L. Smith (Indiana Univ., Bloomington, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1043–1045.—Low concn. of Cl′, Br′ and I′ can be determined rapidly and accurately by direct potentiometric titration with 0·02 *N* $AgNO_3$ (*cf.* Clark, *J.*

Chem. Soc., 1926, 749) in 0·2 *M* acetate buffer containing a few drops of liquid non-ionic detergent to stabilise the system. The equivalence-point potential is determined from the curve of change of potential *vs.* ml of titrant. For halide concn. of $\simeq$ 0·002 *M* the error is $<$ 0·1 per cent., whilst at the limiting concn. of 10^{-4}, 10^{-5} and 10^{-6}, respectively, for Cl′, Br′ and I′, the error is $<$ 1 per cent. Mixed halides can be titrated similarly in a soln. of 0·6 *M* acetate buffer. W. J. BAKER

3039. **Differential spectrophotometric determination of fluoride.** J. J. Lothe (Central Inst. Ind. Res., Blindern, Oslo, Norway). *Anal. Chem.*, 1956, **28** (6), 949–953.—Based on theory developed previously (*Anal. Abstr.*, 1956, **3**, 334), a differential procedure for the indirect spectrophotometric determination of $>$ 200 μg of F′ with Th - alizarin red S at pH 2·80 and 525 mμ (10-mm cell) is described. The extinction of the sample soln. is measured against one of three reference standards containing, respectively, 50, 100 and 200 μg of F′ per 50 ml. Since the accuracy depends mainly on rigid control of pH, the samples are neutralised (in the presence of 0·03 *N* chloroacetic acid as buffer) with 0·05 *N* $HClO_4$, with *p*-nitrophenol as indicator. The error ranges from 0·3 to 0·7 per cent. and the min. limit of determination is $\simeq$ 20 μg of F′. The optimum concn. of the colour reagent and the effect of foreign ions are discussed. W. J. BAKER

3040. **The determination of microgram quantities of fluoride. IV. The use of the aluminium - Eriochrome cyanine complex.** B. J. MacNulty, G. J. Hunter and D. G. Barrett (Min. of Supply, Kidbrooke, London). *Anal. Chim. Acta*, 1956, **14** (4), 368–380.—This spectrophotometric method depends on the destruction of the aluminium - Eriochrome cyanine complex (**I**) by fluoride solutions free from interfering ions or by fluorosilicic acid. As little as 0·02 μg of F′ per ml can be detected and with up to 20 μg in the final soln. F′ can be determined with an accuracy of $\pm$0·6 μg. *Procedure*—To a neutral solution of fluoride contained in a 50-ml flask and to an equal portion of blank solution in a second flask are added a solution of acetate buffer of pH 4·5 (2 ml). To each flask is added a soln. of **I** (15 ml) prepared from water (450 ml), NH_4Cl (13·4 g), glacial acetic acid (1 ml), 0·25 per cent. Eriochrome cyanine soln. (20 ml) and a standard soln. of alum (111 μg of Al per ml) (10 ml). The flasks are heated at 60° C for 15 min., then cooled to room temp., and the extinctions are measured at 535 mμ. Fluoride is calculated from a calibration curve. C. A. SLATER

3041. **The determination of microgram quantities of fluoride. V. The use of the aluminium - Chromazurol-S complex.** B. J. MacNulty and L. D. Woollard (Chemical Inspectorate, Min. Supply, Kidbrooke, London). *Anal. Chim. Acta*, 1956, **14** (5), 452–456.—Fluoride ions are determined by measuring their decolorising effect on the Al - Chromazurol-S complex. *Procedure*—Separate the F′ from interfering ions (*cf. Brit. Abstr. C*, 1953, 499) by the method of Willard and Winter (*Brit. Abstr. A*, 1933, 242). Neutralise the distillate (160 ml) with 0·1 *M* NaOH or, if the distillate or soln. contains acid equiv. to $>$ 1 ml of *M* acid per 150 ml, neutralise with 9 *M* aq. NH_3, add 1 ml of acetic acid and adjust to pH 4·25 with 9 *M* aq. NH_3. Prepare a blank soln. with a salt concn. and pH similar to that of the test soln. To an aliquot of the soln. that contains $>$ 20 μg of F′ add 2 ml of buffer soln., pH 4·25 (*vide infra*) and 15 ml of Al - Chromazurol-S soln. (*vide infra*), dilute to 50 ml, heat for 15 min. in a water bath at 60° C and cool in cold water. Determine the extinction in a Spekker absorptiometer with a 2-cm cell and a 605 filter and use, as a comparison soln., an aliquot of the blank soln. similarly treated. Prepare a calibration graph by applying the same procedure to aliquots of standard NaF soln. The buffer soln. is prepared by dissolving 32 g of NH_4Cl in 200 ml of water, adding 40 ml of acetic acid and 10 ml of aq. NH_3 (sp. gr. 0·88), adjusting to pH 4·25, diluting to 300 ml and re-adjusting the pH if necessary. The Al - Chromazurol-S soln. is prepared by dissolving 13·4 g of NH_4Cl in 425 ml of water, adding 3 ml of acetic acid, 25 ml of 5 per cent. gum acacia soln., 20 ml of 0·275 per cent. soln. of Chromazurol-S in 0·01 *M* HCl, 10 ml of standard Al soln. (1 ml $\equiv$ 111 μg of Al) and sufficient 1·8 *M* aq. NH_3 to bring the pH to 4·25, and diluting to 500 ml with water. The accuracy of the method is $\pm$ 0·6 μg of F′ and the limiting concn. in which F′ can be detected is 0·02 μg per ml.

W. C. JOHNSON

3042. **Chemical analysis by ultra-violet filter photometer. II. Determination of small amounts of chloride.** Takeshi Kato and Koichiro Shinra (Dept. of Chem., Kita College, Osaka Univ., Toyonaka, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (2), 245–248.—A small amount of Cl′ ($<$ 100 μg per ml) reacts with Ag_2CrO_4, and CrO_4'', equiv. in amount to the Cl′, are liberated in the aq. soln. and can be photometrically determined at 405 mμ. The optimum pH for the reaction is 5·3 to 7·5 and that for the extinction measurement is 7·6 to 10·8. A significant error results from the presence of Al, Fe, Br′, I′, S″, SCN′, Pb and Ba. The sample (natural water, 50 to 70 ml) is treated with *M* ammonium acetate (5 ml) and Ag_2CrO_4 (300 mg) and made up to 100 ml. The soln. is filtered and a portion is made ammoniacal with 4 *N* aq. NH_3 soln. (0·25 ml) before measuring the extinction. K. SAITO

3043. **Coulometric titrations with electrolytically generated mercury (I and II). Determinations of chloride, bromide and iodide.** E. P. Przybylowicz and L. B. Rogers (Mass. Inst. Technol., Cambridge, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 799–802.—Procedures are given for the potentiometric titration of halides with $Hg^{\cdot}$ generated at 100 per cent. current efficiency from mercury-coated gold and mercury-pool electrodes. Similar indicator electrodes are used, or even a mercury-coated silver generator electrode, as the end-point break is nearly the same and is much larger than that for pure Ag. The sensitivity of these electrodes is discussed. With either a mercury-coated gold or silver electrode, the lower limits for determining (to within $\pm$ 1 per cent.) any halide in a vol. of $\simeq$ 55 ml are Cl′ 0·24 mg (10^{-4} *M*), Br′ 0·067 mg (6×10^{-5} *M*) and I′ 0·038 mg (6×10^{-6} *M*). Smaller amounts can be determined to within $\pm$ 5 per cent. The supporting electrolyte is 0·5 *M* $NaClO_4$ plus 0·02 *M* $HClO_4$, 5 ml of this soln. being added to 50 ml of the diluted sample soln. The equivalence-point potential is obtained by determining the potential between the point of max. change of slope in the potentiometric curve and subtracting 0·18 V from it. In analysing mixtures of halides by this method there are errors due to co-pptn. and formation of

mixed crystals, but the usual adsorption errors in the titration of I′ alone are absent.

W. J. BAKER

3044. **Inorganic complexes in volumetric analysis. I. Use of ferric oxalate complex in the estimation of iodide.** J. V. S. Ramanjaneyulu and B. K. Shukla (Central Salt Res. Inst., Bhavnagar, India). *Z. anal. Chem.*, 1956, **151** (1), 31–33.—A method useful for the determination of I′ in iodised salt (containing 60 to 250 p.p.m. of I) is detailed. Oxidation of HI with excess of Cr_2O_7'' quant. liberates I. The excess of Cr_2O_7'' is reduced by $Fe^{••}$ (excess) and the $Fe^{•••}$ formed are complexed with oxalate so that they cannot interfere in the determination of I. The oxalate catalyses the Cr_2O_7'' - HI reaction. Good agreement with the standard iodate method is attained. *Procedure*—Dissolve the salt (5 to 10 g) in water (50 ml), add 0·01 *N* $K_2Cr_2O_7$ (5 ml), 4 *N* acetic acid (10 ml) and 0·1 *N* Na oxalate (2 ml), and set the mixture aside for 10 to 15 min. Then add 0·01 *N* $Fe(NH_4)_2(SO_4)_2$ (6 ml) and 0·1 *N* KI (a few ml) and titrate the free I with 0·002 *N* $Na_2S_2O_3$.

II. Use of ferric phosphate complex in the estimation of iodide. J. V. S. Ramanjaneyulu and B. K. Shukla. *Ibid.*, 1956, **151** (1), 34–36.—The Fe^{III} - phosphate complex is very stable and can, with advantage, replace the Fe^{III} - oxalate complex (*cf.* Part I, above) in the determination of I′ when interference by Fe^{III} is to be excluded. Some oxalate, however, is still required as catalyst for the Cr_2O_7'' - HI reaction.

III. Use of ferric fluoride complex in the estimation of iodide. J. V. S. Ramanjaneyulu and B. K. Shukla. *Ibid.*, 1956, **151** (3), 184–187.—Another modification is the use of NaF as complexing agent in place of oxalate or phosphate. The method has been applied to the determination of iodide in iodised salt. *Procedure*—Dissolve the sample (5 to 10 g) in H_2O (50 ml) and mix with 0·01 *N* $K_2Cr_2O_7$ soln. (5 ml), acetic acid (1 : 4) (10 ml) and 0·1 *N* sodium fluoride soln. (1 ml). After 5 or 10 min., add 0·01 *N* $Fe(NH_4)_2(SO_4)_2$ soln. (6 ml) and KI soln. and titrate with standard 0·002 *N* $Na_2S_2O_3$ soln.

J. P. STERN
A. R. ROGERS

3045. **Determination of periodic acid in the presence of iodic acid.** Shigeo Hara (Osaka Ind. Res. Inst., Saida-cho, Ikeda, Osaka). *Japan Analyst*, 1956, **5** (3), 163–164.—The use of vanadyl sulphate standard soln. for the direct titration of HIO_4 in the presence of HIO_3 is suggested. A quant. oxidation of $MnSO_4$ to $HMnO_4$ is effected by HIO_4 in $> 10\ N$ H_2SO_4 containing $\simeq$ 10 per cent. H_3PO_4 by boiling for 5 min. The product is cooled and titrated with *N*/30 $VOSO_4$. The presence of HIO_3 has no adverse effect.

K. SAITO

3046. **End-point identification in manganese titration by the Volhard - Wolff method.** G. Talsky. *Angew. Chem.*, 1956, **68**, 182.—It is found that the end-point in the titration of manganese by the Volhard - Wolff method (direct oxidation with $KMnO_4$ to MnO_2 in the presence of $ZnSO_4$ and ZnO) is most easily observed if a pocket spectrometer, with the green part of the spectrum, is used.

C. A. FINCH

3047. **Improved photo-electric determination of iron in alloys with dimethylglyoxime.** Hiroshi Iinuma and Takayoshi Yoshimori (Faculty of Eng., Gifu Univ., Naka-machi, Gifu Prefecture). *Japan Analyst*, 1956, **5** (3), 149–152.—The extinction and stability of the $Fe^{••}$ complex of dimethylglyoxime (**I**) are dependent on the kind and amount of reducing agent. When a mixture of vanadyl sulphate (**II**) and hydroxylamine (**III**) is used the colour develops in 15 min. and then remains unchanged for 45 min. No significant error results from the presence of Co (< 0·2 mg), Pb (< 0·5 mg), Mn (< 0·5 mg), Cr (< 0·5 mg), Sn (< 1 mg), Mg (< 10 mg), Sb (< 10 mg), Ti (< 20 mg), Al (< 50 mg) and Zn (< 100 mg) in 100 ml. Copper interferes with the coloration of $Fe^{••}$ with **I** and should be removed by shaking with liquid zinc amalgam (**IV**) before the addition of **I**. Aluminium alloys (0·1 to 0·2 g) are dissolved in NaOH (20 per cent., 5 to 8 ml), diluted and filtered. The residue is dissolved in HCl (1 + 1, 10 ml) and H_2O_2 (10 per cent., 1 to 2 ml) and made up to 100 ml. A 5- or 10-ml portion is treated with **II** (0·02 *N*, 2·0 ml), shaken with **IV** for a few min. and transferred to a 100-ml calibrated flask with **III** (10 per cent., 3 to 4 ml), Na K tartrate (40 per cent., 3 to 4 ml), **I** (1 per cent. in ethanol, 3 to 4 ml) and conc. aq. NH_3 soln. (6 to 10 ml). The soln. is made up to vol. with water and submitted to colorimetry at 530 mμ. Copper alloys (0·5 to 0·8 g) are dissolved in HCl (1 + 1, 20 to 30 ml) and H_2O_2 (10 per cent., 1 to 2 ml), then heated with H_2SO_4 (1 + 1, 10 ml) to white fumes, dissolved in water (70 ml), and filtered. The filtrate is electrolysed to remove most of the Cu and made up to 250 ml before being treated as described above.

K. SAITO

3048. **A quick and precise heterometric determination of iron with aluminon in excesses of foreign metals.** M. Bobtelsky and A. Ben-Bassat (Hebrew University, Jerusalem, Israel). *Anal. Chim. Acta*, 1956, **14** (5), 439–445.—The heterometric titration of $Fe^{•••}$ is improved by the addition of $Cr^{•••}$, which also make the titration possible in the presence of a high proportion of $Al^{•••}$. *Procedure*—To 10 ml of a soln. containing 0·2 to 0·5 mg of $Fe^{•••}$ add 1 ml of *M* acetic acid and 1 to 2 ml of *M* $Cr(NO_3)_3$ and titrate heterometrically (*cf. Anal. Abstr.*, 1954, **1**, 1770) with 0·003 *M* to 0·006 *M* aluminon. The method serves also for the titration of $Fe^{•••}$ in the presence of relatively high concn. of salts of the following metals—Pb, Cd, Cu, Co, Ni, Mn, Zn, Mg, Ba and Ca.

W. C. JOHNSON

3049. **Determination of metallic iron in iron catalysts containing both ferrous and ferric oxides.** Yoshio Murata and Shigeaki Kasaoka (Coll. Educ., Osaka Prefectural Univ., Mozu-higashino-machi, Sakai, Osaka). *Japan Analyst*, 1956, **5** (3), 156–159.—The dissolution of metallic Fe in a mixture with FeO, Fe_2O_3 and Fe_3O_4 was studied by the use of $CuSO_4$ and $HgCl_2$; $CuSO_4$ appears to dissolve a part of FeO, and thus gives high values for metallic Fe. A reproducible result is provided when the sample is refluxed at 95° C (10 to 20 min.) with a neutral soln. of $HgCl_2$ (3 to 6 per cent.; the total $HgCl_2$ should be $\simeq$ 10 times the weight of the metallic iron), and titrated with $KMnO_4$ in a soln. containing H_2SO_4 and H_3PO_4. For an accurate analysis (error < 0·5 per cent. absolute), a preliminary approximate estimation of metallic Fe should be made.

K. SAITO

3050. **Contribution to micro-methods in iron research.** H. Malissa (Max-Planck Inst. f. Eisenforsch., Düsseldorf, Germany). *Mikrochim. Acta*,

1956, (1–3), 474–484.—Techniques are described for the separation and analysis of individual compounds occurring in iron, *e.g.*, nitrides, carbides and oxides. D. F. PHILLIPS

3051. **An improvement of the colorimetric determination of silicon in iron and steel.** Kiichi Narita Developing Dept., Kobe Seiko-sho, Nada-ku, Kobe). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (2), 270–274.—The reaction of SiO_2 with molybdic acid was studied and a modification of the conventional colorimetric determination of Si in iron and steel is suggested. The improvement consists in removal of Fe, Cr, Ni and Co by mercury-cathode electrolysis at pH 1; these metal ions cause marked interference in the colorimetry. Since SiO_2 can be present in various modifications, including some that are insol. in dil. HCl, the residue from the H_2SO_4 soln. of the sample should be fused with Na_2CO_3 to recover SiO_2 that is reactive with molybdic acid. The new method enables an accurate estimation of 0·001 to 1 per cent. of Si to be effected. K. SAITO

3052. **Polarographic determination of arsenic in iron and steel.** Masao Yana, Heiichi Mochizuki, Rokuro Kajiyama and Yoshiaki Koyama (Nippon Yakin Kogyo Co., Ltd., Daishigawara, Kawasaki). *Japan Analyst*, 1956, **5** (3), 160–163.—The polarographic reduction of As^{III} was examined in various supporting electrolytes with reference to its application to the analysis of iron and steel. In an aq. soln. containing N HNO_3 and 2 M NaCl, a two-step wave is observed ($E_{\frac{1}{2}} = -0{\cdot}40$ and $-0{\cdot}65$ V *vs.* the S.C.E.). The wave height of the first is proportional to the amount of As within the range 0·1 to 10 mg per 100 ml. The addition of a max. suppressor such as gelatin or methylene blue was found not to be essential. Arsenic is separated from other ingredients in iron and steel by reduction to the elementary state with $SnCl_2$, and is then dissolved in HNO_3 (1 + 1, 15 ml). After the addition of NaCl (10 g) and gelatin (0·2 per cent., 2 ml), the soln. is made up to 100 ml with water and submitted to polarography. K. SAITO

3053. **The determination of nitrogen in austenitic steels using a cyanogen band head.** E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Mich., U.S.A.). *Applied Spectroscopy*, 1956, **10** (2), 68–70.—A spectrographic method is given for the determination of N in steel over the range 0·4 to 0·8 per cent. The sample is in the form of a disc (1 cm diam., 4 mm thick) which is arced as the anode in a 16-amp. d.c. arc *vs.* a graphite rod. The arc is surrounded by a CO_2 atmosphere in a suitable gas chamber, which is described. An échelle grating attachment crossed with a large Littrow quartz spectrograph is used to give sufficient resolution of Cr 3883·29 A and the CN band head 3883·56 A, which is compared with Fe 3865·53 A as the internal standard. The accuracy is within ± 10 per cent. of the amount present. P. T. BEALE

3054. **Quadrivalent uranium as a reducing agent in potentiometric titrations. I. Estimation of ferric and ceric salts.** I. M. Issa and I. M. El Sherif (Cairo Univ., Giza, Egypt). *Anal. Chim. Acta*, 1956, **14** (5), 466–473.—Solutions of U^{IV} are produced by reducing soln. of UO_2SO_4 in the Jones reductor or electrolytically. It has been confirmed that the stability of such soln. increases with increase of acidity. The redox potential of the U^{VI} - U^{IV} system has been measured in 0·1 to 8 N HCl and in 0·1 to 15 N H_2SO_4. Ferric chloride is titrated potentiometrically with 0·14 N U^{IV} soln. in 0·1 to 7 N HCl, and ferric alum is titrated in 0·1 N H_2SO_4 and in 2·7 N HNO_3. At the higher acidities and at room temp., up to 14 min. may be required to reach equilibrium at the end-point, but at 60° C the reaction is more rapid. Suitable conditions have been devised for the titration of $Fe(CN)_6'''$ and $Ce^{\cdot\cdot\cdot\cdot}$, these reactions being accelerated by the addition of $Fe^{\cdot\cdot\cdot}$. In 0·36 N H_2SO_4 the components of the following mixtures can be titrated individually—$Ce^{\cdot\cdot\cdot\cdot}$ - $Fe^{\cdot\cdot\cdot}$, VO_3' - $Fe^{\cdot\cdot\cdot}$, and VO_3' - $Ce^{\cdot\cdot\cdot\cdot}$ - $Fe^{\cdot\cdot\cdot}$.

II. Estimation of dichromate, permanganate, bromate and tellurate. I. M. Issa and I. M. El Sherif. *Ibid.*, 1956, **14** (5), 474–481.—Dichromate can be titrated with a soln. of U^{IV} in the presence of HCl or H_2SO_4. Mixtures of Cr_2O_7'' with $Ce^{\cdot\cdot\cdot\cdot}$ or VO_3' yield a single inflection that corresponds to the sum of the components. Dichromate and $Fe^{\cdot\cdot\cdot}$ yield separate inflections. Permanganate can be titrated with a soln. of U^{IV} in 0·1 to 2 N H_2SO_4. The titration proceeds in two stages, first to MnO_2 and then to $Mn^{\cdot\cdot}$; in 0·7 to 2 N H_2SO_4 the separation of MnO_2 is inhibited. In alkaline soln. MnO_4' cannot be reduced quant. to MnO_4'' with U^{IV}, but the reduction proceeds quant. to MnO_2 in 1·5 to 3 N NaOH. In 0·3 N H_2SO_4, MnO_4' and $Fe^{\cdot\cdot\cdot}$ can be titrated separately in the same soln.; MnO_4', Fe and VO_3' can also be titrated separately. Mixtures of Cr_2O_7'' and VO_3', and of MnO_4', $Ce^{\cdot\cdot\cdot\cdot}$ and Cr_2O_7'', yield curves with only one inflection representing the sum of the components. Conditions are also specified for the titration of BrO_3' and TeO_4'', respectively. W. C. JOHNSON

3055. **Determination of ferricyanide with ascorbic acid.** L. Erdey and G. Svehla (Tech. Univ., Budapest). *Z. anal. Chem.*, 1956, **150** (6), 407–415.—Ferricyanide soln. can be titrated at pH 5 to 6 with standard ascorbic acid (**I**), either potentiometrically or with 2:6-dichlorophenolindophenol (**II**) as indicator. The simplicity of the method is very advantageous. The accuracy for 0·1 to 1·0 N soln. is within ± 0·3 per cent. *Procedure*—(*a*) To 20 ml of the $K_3Fe(CN)_6$ soln. add Na acetate (5 g). Titrate with 0·1 N **I**, with a platinum indicator-electrode and a S.C.E. The end-point can be checked visually (disappearance of yellow colour). (*b*) To the neutral $K_3Fe(CN)_6$ soln. add Na acetate (5 g per 100 ml) and 0·1 per cent. **II** soln. and titrate with 0·1 N **I**. Near the end-point the greenish colour changes to azure, and at the end-point it disappears. J. P. STERN

3056. **The titration of nickel with EDTA at pH 2·8.** K. ter Haar and J. Bazen (Philips' Gloeilampenfabrieken, Eindhoven, Netherlands). *Anal. Chim. Acta*, 1956, **14** (5), 409–413.—*Procedure*—To the soln., containing 30 to 120 mg of $Ni^{\cdot\cdot}$, add a small excess (1 to 5 ml) of 0·05 M EDTA (disodium salt), dilute to 100 ml, neutralise to Congo-red paper with 2 N aq. NH_3, add 5 ml of 2 M chloroacetic acid and 5 ml of M Na acetate. Adjust the pH to between 2·7 and 2·9 with 2 N aq. NH_3 or 2 N HCl. Add 1·5 ml of 0·1 per cent. aq. alizarin red S and immediately titrate with 0·05 M $Th(NO_3)_4$ to a colour change from green to brown. In the presence of 20 mg of Co, results are high by ≃ 1 per cent. Zinc interferes to the same extent as does Co; Pb has a greater influence, and Cu, Al

and Fe must be absent; Mn does not interfere. The formation constant of the Th^{IV} complex of EDTA has been determined at pH 2·5 to 3·0, by measuring the decrease in the extinction of a soln. of the Ni complex when $Th^{\cdots\cdot}$ are added. A value of $10^{-19\cdot8}$ is obtained. W. C. JOHNSON

3057. **Method of estimating metallic nickel in the presence of nickel oxides in complex materials (minerals).** C. Ek (Univ. Liège, Belgium). *Anal. Chim. Acta*, 1956, **14** (4), 311–317.—Two methods are described for the estimation of nickel in the presence of nickel oxides in complex materials such as ores. *Procedure*—(*i*) A 1·85 per cent. w/v soln. of $HgCl_2$ (100 ml) is heated under reflux and to it is added powdered ore containing not more than 0·1 g of metallic nickel. Boiling is continued for 2 hr. The soln. is cooled and filtered and Ni is estimated by electrolysis of the filtrate after separation of mercury and other elements. (*ii*) This method is similar to method (*i*), but the $HgCl_2$ soln. is replaced by a mixture of $HgCl_2$ (1·85 per cent. w/v; 100 ml), KCN (8 per cent. w/v; 25 ml) and sufficient 6 *N* HCl to give a final pH of 9. In this case it is necessary to boil for 6 hr. The method has an accuracy of about ± 5 per cent.
C. A. SLATER

3058. **Photometric nickel determination with sodium dimethylglyoxime.** W. Nielsch and L. Giefer (Riedel-de Haën A.-G., Seelze, Hanover, Germany). *Mikrochim. Acta*, 1956, (1–3), 522–527.—It is shown that ≮ 5 μg of Ni can be quant. pptd. with the water-soluble Na dimethylglyoxime. The Ni complex is extracted with chloroform. After drying it is subjected to photometry in the Zeiss Elko II apparatus in conjunction with a mercury lamp and a S 38E filter. The procedure for determination of Ni in Fe and its compounds is described. D. F. PHILLIPS

3059. **The analysis of metallic nickel. V. Determination of aluminium.** Shigeru Yokosuka (Bessi Mine Office, Sumitomo Metal Mining Co., Ltd., Niihama). *Japan Analyst*, 1956, **5** (2), 71–74.—The photometric determination of Al (< 50 μg) by the oxine extraction method was studied in the presence of Mn and Pb (< 500 μg) and its use in the analysis of metallic nickel is suggested. The extraction of Al oxinate with benzene from an ammonium acetate buffer (pH 9) containing tartrate and cyanide is not affected by metal ions other than Mn (> 200 μg) and Pb. When the benzene extract of Al and Pb oxinates is shaken with acetate buffer of pH 5, Pb oxinate is transferred to the aq. layer. *Procedure*—The sample soln. [about 1 g of Ni, in HNO_3 (1 + 1)] is treated with tartaric acid (10 per cent., 2 ml) and sufficient aq. NH_3 soln. (1 + 1) to convert all the Ni into the ammine complex. The product is then converted into the cyano complex with KCN (30 per cent.) and the pH value is adjusted to 9·0 ± 0·2 with acetic acid and aq. NH_3 soln. after the addition of Na_2SO_3 (saturated aq. soln., 5 ml) and oxine (1 per cent. in dil. acetic acid, 2 ml). The soln. is extracted with benzene (20 ml) for 1 min.; the benzene layer is washed with an acetate buffer of pH 4·5 (20 ml) and its extinction is measured at 395 mμ. In the presence of considerable amounts of Mn (0·02 to 0·8 per cent.) the sample soln. in H_2SO_4 is submitted to mercury-cathode electrolysis and the soln. (free from Mn, Ni, etc.) is adjusted to pH 5·5 before being photometrically determined (525 mμ) with aluminon.

VI. Determination of calcium. Shigeru Yokosuka. *Ibid.*, 1956, **5** (2), 74–77.—After the removal of Ni and minor constituents by mercury-cathode electrolysis or by ion exchange, Ca (>0·0002 per cent.) is determined by flame photometry in a 0·3 *N* HCl soln. containing 40 per cent. methanol. When the intensity of the Ca line is measured at 554 mμ, the presence of metals other than Al (> 2 p.p.m.) causes no appreciable interference. Since Al markedly decreases the intensity, it should be removed by the oxine - benzene method. *Procedure*—The sample (2·5 g) is dissolved in HNO_3 (1 + 1, 30 ml), heated with H_2SO_4 (1 + 2, 10 ml) to white fumes, and dissolved in water (60 ml). The soln. is adjusted to a pH of 1 to 2 and electrolysed, with a mercury cathode, as described in Part III (*cf. Anal. Abstr.*, 1956, **3**, 47). The resulting soln. is evaporated to dryness, dissolved in 5 *N* acetic acid (2 ml) and water (30 ml) and treated with 5 *N* aq. NH_3 soln. and 2 per cent. oxine to make the pH 9·0. It is then extracted with benzene, evaporated and dissolved in *N* HCl and methanol and submitted to flame photometry. For ion-exchange separation, the HNO_3 soln. of the sample is treated with enough aq. NH_3 soln. (1 + 1) and NaCN (1 per cent.) to convert all the Ni into the cyano complex. The soln. is made up to 2 litres and passed through a column of Amberlite IR-120 (5 ml per min.) which is washed with water (50 ml) and successively eluted with 0·5 *N* HCl (200 ml, 3 ml per min.) and 4 *N* HCl (70 ml, 2 ml per min.). The 4 *N* HCl soln. is evaporated to dryness, the residue is dissolved in *N* HCl (15 ml) and the soln. is submitted to flame photometry. K. SAITO

3060. **The extraction and determination of small quantities of nickel dimethylglyoxime with chloroform. The determination of nickel in copper salts.** W. Nielsch (Riedel-de Haën, A.-G., Seelze, Hanover, Germany). *Z. anal. Chem.*, 1956, **150** (2), 114–118.—Nickel dimethylglyoxime can be extracted by a single extraction with chloroform from aqueous solution at pH 6·5 and 8·9 at concn. > 2 μg per ml. Interference due to copper is overcome by the addition of $Na_2S_2O_3$ at pH 6·5. Nickel in $Cu(NO_3)_2$ or Cu acetate can be estimated. Dissolve 1 g of a copper salt in water (10 ml) in a 100-ml separator and add Na tartrate (0·5 g), $Na_2S_2O_3$ (5 g), Na acetate buffer (30 per cent. Na acetate adjusted to pH 6·5 with 30 per cent. acetic acid) (5 ml) and hydroxylamine hydrochloride (50 mg), shaking vigorously after each addition. Add dimethylglyoxime solution (1 per cent. in alcohol) (2 ml) and chloroform (6 ml), shake for 1 min., allow to separate, and filter the chloroform layer into a cell. Measure the absorption at 366 mμ and determine the amount of Ni present from a calibration curve. P. S. STROSS

3061. **Spectrographic determination of rhodium in platinum - rhodium alloys.** Á. Bardócz and F. Varsányi (Central Res. Inst. Physics, Budapest, Hungary). *Anal. Chem.*, 1956, **28** (6), 989–993.—A spectrographic procedure for determining from 1 to 25 per cent. of Rh in Pt - Rh alloys by soln. excitation with a rotating-pin electrode is described fully. The sample soln. is transferred to the spark gap (1 mm) on carbon electrodes, fixed like spokes on a slowly rotating shaft, and afterwards passing before a fixed counter-electrode on which spark excitation starts. The spark source is electronically controlled (1000 V, 4 microfarads, 4 ohms), the effective pre-sparking and exposure times being 7·5 and 15 sec., respectively. Measurements are made in a Zeiss high-speed microphotometer (slit

width 0·4 mm, slit height 20 mm), with the line pairs Rh 3434·89 - Pt 3408·13 A and Rh 3396·85 - Pt 3408·13 A, for each of which standard curves are previously prepared. Reproducibility is within ± 1·9 per cent. and the mean error is ≃ ± 2·8 per cent. The rotating-pin-electrode technique eliminates the problems of porosity and warming-up inherent in the porous-cup-electrode method.

W. J. BAKER

3062. **Analytical aspects of some organic compounds. II. Determination of palladium by 4-aminosalicylic acid.** Sachindra Kumar Datta (Darjeeling Gov. Coll., India). *J. Indian Chem. Soc.*, 1955, **32** (12), 785–790.—Gravimetric and colorimetric methods are described. The reagent gives with Pd at pH 3·7 a quant. ppt. of a yellow complex corresponding to the formula $Pd(C_7H_6O_3N)_2$. Separation of Pd from Zn, Al, Mg, Cu, Ca, Ba, Sr, Co, Ni, Pt, Au and V can be effected with this method; Fe, Ti, Zr and Th interfere, but Ti can be masked with sulphosalicylic acid. The Pd can be estimated by direct weighing of the complex, or volumetrically by bromination with KBr - $KBrO_3$ after decomposing the complex.

I. JONES

3063. **Colorimetric determination of osmium (VI) with 1-naphthylamine-3:5:7-trisulphonic acid.** H. C. Wingfield and J. H. Yoe (University of Virginia, Charlottesville, U.S.A.). *Anal. Chim. Acta*, 1956, **14** (5), 446–451.—1-Naphthylamine-3:5:7-trisulphonic acid forms a violet complex with Os^{VI} in weakly acid soln. The reaction is sensitive to 1 pt. of Os^{VI} in $1·5 \times 10^7$ pt. of soln. The colour is sensitive to pH change; it shows a max. intensity at pH 1·5 with an absorption max. at 560 mμ. Max. intensity is reached after 4 hr.

W. C. JOHNSON

See also Abstracts 2944, 2945, 2946, 2952, 2954, 2961, 3067, 3093, 3199, 3211, 3214, 3224, 3242, 3246.

3.—ORGANIC ANALYSIS

3064. **The use of the mass spectrometer for the identification of organic compounds.** J. H. Beynon [I.C.I. (Dyestuffs Div.) Research Lab., Manchester]. *Mikrochim. Acta*, 1956, (1–3), 437–453.—A method of deducing the molecular structure of organic compounds from their mass spectra obtained from < 1 mg of material is described. The technique is limited to compounds whose vapours do not decompose at pressures of 10^{-5} to 10^{-6} mm (Hg). Details of the gas-sample handling system are described. Interpretation of the mass spectra, although simpler with pure substances, usually gives information as to whether the sample is a mixture or not and in simple cases can lead to identification of the components. The use of vapour-phase chromatography for preliminary separation before mass-spectrometric analysis of more complex mixtures is mentioned. Examples of applications are given. The very wide range of peak heights (1 to 10^5) which can be dealt with sometimes enables impurities present at a few p.p.m. to be identified and measured.

D. F. PHILLIPS

3065. **Application of vapour-phase chromatography to mass-spectrometer analysis.** C. M. Drew, J. R. McNesby, S. R. Smith and A. S. Gordon (U.S. Naval Ordnance Test Sta., China Lake, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 979–983.—Apparatus and procedures are described for the partial or complete separation of gaseous mixtures (*e.g.*, hexane isomers, or a mixture of propylene, propyne and allene) by vapour-phase chromatography, with simultaneous recovery of a part of each separated fraction for mass-spectrometric analysis. Solid absorbents (silica gel, activated C) or partition columns (paraffin oil on Celite) can be used, though the latter have greater advantages (less tailing, elution at much lower temp., and wider applicability). Satisfactory resolution can be obtained with columns 32 ft. long, 7 mm diam., with He as carrier gas (flow rate 20 to 40 cu. cm per min.), operating between 0° and 100° C (65° C for hexane isomers). With a silica-gel column, 8 ft. by 3 mm, with the flow rate of 50 cu. cm per min., a complete separation of 0·05 cu. cm of a mixture of ethane, propane and butane into three pure fractions can be made. The method is particularly suited to the analysis of a mixture of a hydrocarbon and its deuterated derivatives.

W. J. BAKER

3066. **Identification of organic compounds by microscopy and X-ray diffractometry.** J. Mitchell, jun., and A. L. Ryland (E. I. du Pont de Nemours & Co. Inc., Wilmington, Del., U.S.A.). *Mikrochim. Acta*, 1956, (1–3), 422–436.—Identification of crystalline organic compounds is being increasingly accomplished through measurement of their primary and secondary crystallographic constants by means of the microscope and X-ray diffractometer. Those constants measurable under the microscope include optic axial angle, character, dispersion and refractive indices and extinction directions. Crystalline materials can be identified by X-ray diffraction determinations of "d" spacings and intensities. Comparative studies of the use of both microscopic and X-ray techniques for the identification of mixtures of the *p*-bromoanilides of acetic and propionic acids and also of the 2:4-dinitrophenylhydrazones of acetaldehyde and propionaldehyde are discussed. (42 references.) D. F. PHILLIPS

3067. **Use of silver permanganate in analysis. IV. Micro-estimation of carbon and hydrogen.** J. Körbl and K. Blaboil (Res. Inst. Pharm. and Biochem., Czech. Acad. Sci., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (2), 318–321.—The previously described method for the semi-micro determination of C and H, with the decomposition product of $AgMnO_4$ as catalyst (*cf. Anal. Abstr.* 1956, **3**, 733) is applied to micro-determinations. The same apparatus is used, and the catalyst (a 3·5-cm layer) is contained in a hard-glass tube (10-mm diameter). *Procedure*—The sample (≃ 4 mg) is burned for 5 min. in a stream of O (8 ml per min.), and then the apparatus is flushed out with 80 to 100 ml of O. The absorption vessels are wiped with a moist flannel rag and then cleaned with two pieces of leather. The zero position of the balance is taken within 6 min. The H_2O-absorption vessel is suspended from the beam in the sixth min. and its wt. is taken during the tenth min. The CO_2-absorption vessel is laid on the balance during the eleventh min. and its wt. taken during the fifteenth min. The determination requires 45 min., and gives an absolute error of + 0·11 per cent. for C and + 0·22 per cent. for H.

V. Complexiметric estimation of combustible sulphur as manganous - sulphate. J. Körbl and R. Přibil. *Ibid.*, 1956, **21** (2), 322–326.—When the decomposition product of $AgMnO_4$ is used as

a catalyst in combustion analyses, combustible S is absorbed quant. as Ag_2SO_4 and $MnSO_4$. The determination of the SO_4'' as $BaSO_4$ is time consuming, so a compleximetric estimation of the metals is investigated. Manganese can readily be estimated with EDTA (disodium salt) and Eriochrome black T, so the Ag^+ are first converted into an equiv. amount of Mn^{++}, according to the reaction—

$$2Ag^+ + MnO_2 + 2H_2O_2 = 2Ag + Mn^{++} + 2H_2O + 2O_2.$$

The H_2O_2 is introduced in the form of urea hydrogen peroxide. *Procedure*—With the microtrain already described (*cf. Anal. Abstr.*, 1956, **3**, 733) and a 3·5-cm layer of the catalyst previously heated to 500° C, samples of S are burned in a stream of O (20 ml per min.) for 1 to 2 min. The catalyst is extracted, boiled with water, and 0·5 g of urea hydrogen peroxide is added with stirring. More MnO_2 may have to be added if there is an insufficient quantity present in the catalyst. The Mn is then determined by titration with 0·05 *N* EDTA (disodium salt) soln. and, with Eriochrome black T indicator. In this way samples of S in amounts up to 22 mg are estimated in <30 min. with an error of < 0·5 per cent. The method should prove suitable for the estimation of vapours of S as well as of S in organic compounds, pyrites, etc.

J. H. WATON

3068. **Determination of sulphur in organic compounds. I. Volumetric determination with barium chromate.** Yoshimasa Tanaka (Pharm. Faculty, Univ. of Kumamoto, Oemachi, Kuhonji, Kumamoto). *J. Pharm. Soc. Japan*, 1955, **75** (6), 653–655.—Organic compounds are decomposed with fuming HNO_3 in a sealed tube (250° C, 5 hr.), then treated with $BaCrO_4$, and the liberated CrO_4'' are titrated with 0·05 *N* Fe^{++} soln. in the presence of H_3PO_4; Ba diphenylaminesulphonate is used as indicator. This method can be satisfactorily carried out (error < 0·3 per cent.) on a micro (5 to 8 mg) or semi-micro (20 mg) scale.

K. SAITO

3069. **Determination of 20 to 100-micromilligram quantities of organic nitrogen.** D. Exley (Unit for Res. in Cell Metabolism, Dept. of Biochem., Univ. of Oxford). *Biochem. J.*, 1956, **63** (3), 496–501.—An ultra-micro method is described for the determination of organic N. It involves digestion of the sample with H_2SO_4 in the presence of Se as catalyst, and direct determination of the NH_3 formed, after neutralisation of the digest, by the addition of Russell's phenol - hypochlorite reagent (*Brit. Abstr. C*, 1945, 129) and measurement of the intensity of the colour spectrophotometrically at 625 mμ in specially constructed capillary cells. The method is applicable to quantities five times smaller than is any previous method. The standard error of a single determination is not greater than ± 6·5 per cent. at 50 μmg of N or over, and it is ± 8 per cent. for the range 5 to 20 μmg of N. The method is readily applicable to the micro scale, when no special apparatus is needed. Some advantages of the method are that all the reactions up to the final development of colour are carried out in the same tube, the time for digestion is reduced from 6 hr. to 1 hr., and with the use of acid traps much contamination from the air is avoided.

J. N. ASHLEY

3070. **Use of periodic acid for detecting and locating ethylenic unsaturation.** A. Chatterjee and S. G. Majumdar (Univ. Coll. Sci. and Technol., Calcutta, India). *Anal. Chem.*, 1956, **28** (5), 878–879.—Periodic acid can be used for the detection and location of a carbon-to-carbon double-bond. The reaction involves cleavage of the bond and the production of carbonyl derivatives; which can be characterised and estimated as their 2:4-dinitrophenylhydrazones or dimedone deriv. The yield of the aldehydic or ketonic fragments obtained corresponds to that calculated from the number of double-bonds present.

G. P. COOK

3071. **Studies on hydroxamic acids. VI. Colorimetric micro-determination of the carbonyl group (hydroxylamine number).** E. E. Vonesch and O. A. Guagnini (La Plata Nat. Univ., Argentina). *An. Asoc. Quim. Argent.*, 1955, **43** (3), 185–189.—To 2 ml of an approx. 0·1 *N* solution of hydroxylamine hydrochloride in a 25-ml calibrated flask is added a volume of ethanolic KOH solution equal to 85 per cent. of that needed for a blank determination on the hydroxylamine solution, together with 0·7 to 5·0 mg of sample (in 2·5 ml of ethanol), making to volume with aldehyde-free ethanol. The solution is heated on the water bath for 30 min., and the colour is measured by the technique given earlier (*cf. Anal. Abstr.*, 1956, **3**, 448). The difference in colour developed in the blank and in the mixture containing the sample is a measure of the hydroxylamine used in the reaction. The no. of μg of hydroxylamine equivalent to 1 mg of sample is the hydroxylamine number.

L. G. L. UNSTEAD-JOSS

3072. **Hydroxyammonium acetate as carbonyl reagent.** T. Higuchi and C. H. Barnstein (Univ. Wis., Madison, U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1022–1025.—A method for carbonyl determination based on oximation with hydroxyammonium acetate in acetic acid is given. The oximes formed are sufficiently weaker as bases to permit the reagent in acetic acid to be satisfactorily titrated with $HClO_4$, and oximes of some aliphatic and cyclic ketones often possess such intermediate basic strength as to permit them to be directly titrated in the presence of excess of reagent. Analysis of 15 carbonyl compounds gave recoveries of > 97·4 per cent. with reasonable reproducibility. The method is unaffected by large concn. of organic acids of widely differing strengths. A method for the preparation of the reagent and a study of the kinetics of its reaction with a ketone are also included.

G. P. COOK

3073. **The extreme sensitivity of the determination of carbon monoxide, ethylene and acetylene by iodine pentoxide.** M. Picon. *Bull. Soc. Chim. France*, 1956, (2), 370–371.—Air passed over MnO_2, before being passed over I_2O_5 on pumice at 170° C in an apparatus described, liberated iodine equiv. to 1 part in 1,300,000 of CO, ethylene or acetylene. Without passage over the MnO_2, iodine is liberated equiv. to 1 part in ≃ 300,000.

E. J. H. BIRCH

3074. **Polarographic study of alkyl hydroperoxides.** D. A. Skoog and A. B. H. Lauwzecha (Stanford Univ., Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 825–828.—A systematic study of the reduction of 17 typical alkyl hydroperoxides, varying from 4 to 9 carbon atoms in chain length, is described. Water and aq. ethanol were used as solvents and, of several supporting electrolytes investigated, H_2SO_4 was the most satisfactory. The best polarograms were obtained with the compounds of higher

mol. wt., but the half-wave potentials for all the hydroperoxides were so close together that the determination of any single hydroperoxide was impossible. In general, the diffusion currents were directly proportional to concn., but the proportionality constants for the various compounds varied widely and so limited the method for functional group analysis. G. P. COOK

3075. **Spot test for trace ethanol.** F. Feigl and C. Stark (Lab. Prod. Mineral, Min. Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1956, **45** (2), 39–40.—In the two procedures described, ethanol is detected by transforming it to acetaldehyde, which is in turn detected by a blue colour reaction with nitroprusside containing morpholine or piperidine. In (*i*), 3 drops of a soln. composed of equal volumes of 0·1 *N* $KMnO_4$ and H_2SO_4 (1:1) in a micro test-tube are covered with 1 to 3 drops of sample soln. Filter-paper moistened with nitroprusside - morpholine soln. (equal volumes of 5 per cent. sodium nitroprusside soln. and 20 per cent. aq. morpholine soln.) is placed over the tube. A blue stain appears in 2 to 6 min., the time required and depth of colour depending on the ethanol content. In (*ii*), several centigrams of hot copper wire or cupric oxide are dropped on to 1 to 3 drops of the sample in a micro test-tube. Detection of ethanol is the same as in (*i*). By (*i*), 60 μg of ethanol can be detected in 1 drop of benzene - ethanol mixture, and by (*ii*), 3 μg. Some applications are noted. O. M. WHITTON

3076. **Photometric determination of water in ethanol.** J. de Oliveira Meditsch (Esc. Engenharia, P. Alegre, Brazil). *Chemist Analyst*, 1956, **45** (2), 49–50.—The method described depends on the increase in solubility of $K_2Cr_2O_7$ in H_2O - ethanol systems with increase in H_2O content; the dichromate concentration is determined colorimetrically. Excess of $K_2Cr_2O_7$ (5 g) and glacial acetic acid (1 ml) are added to a 50-ml sample of ethanol. After the soln. has been set aside for 20 min., with occasional shaking, the supernatant saturated liquid is separated and its extinction determined at 520 mμ. A calibration curve is prepared. Results presented show that Beer's law is followed in the range of concentration studied, and the effect of temp. O. M. WHITTON

3077. **The detection, characterisation and estimation of aldehydes. I. Methods of oximation.** S. Veibel and I. G. K. Andersen (Tech. Univ., Copenhagen, Denmark). *Anal. Chim. Acta*, 1956, **14** (4), 320–324.—Five methods for the estimation of aldehydes by oximation, among them those of Bryant and Smith (*J. Amer. Chem. Soc.*, 1935, **57**, 57) and Smith and Mitchell (*Anal Chem.*, 1950, **22**, 750), are compared. In all the methods, single or double branching in the α-position in aliphatic aldehydes, or in the 2- and 6-positions in aromatic aldehydes reduces the accuracy of the method because of steric hindrance. C. A. SLATER

3078. **Two volumetric methods for the determination of glyoxal.** P. Salomaa (Univ. Turku, Finland). *Acta Chem. Scand.*, 1956, **10** (2), 306–310.—On the basis of an investigation of the rates and equilibria of the Cannizzaro reaction and the bisulphite addition reaction of glyoxal, two methods have been worked out for its determination. (*i*) To a neutral soln. of glyoxal ($\gtrsim$ 0·66 millimole in $\gtrsim$ 10 ml) is added 0·05 *N* NaOH soln. (20 ml). After 8 min. an equivalent amount of standard HCl is run in and the excess of acid is titrated against 0·05 *N* NaOH, with phenol red as indicator. The amount of NaOH consumed corresponds directly to the glyoxal present. (*ii*) To a soln. of glyoxal (containing $\gtrsim$ 0·75 millimole) are added phosphate buffer (10 ml), containing 0·5 mole of Na_2HPO_4 and 0·125 mole of KH_2PO_4, and 0·1 *M* $NaHSO_3$ (20 ml). If the total volume does not exceed 40 ml, a reaction time of 3 min. is sufficient. After this, *N* HCl (5 ml) is added and the excess of $NaHSO_3$ is titrated with 0·1 *N* I solution. Rapid titration is essential. Both methods give identical results, errors being no greater than the random titration error. C. A. SLATER

3079. **4-Substituted thiosemicarbazides as reagents for the characterisation of aldehydes and ketones. III. 4-*p*-Bromophenylthiosemicarbazide.** M. Tišler (Inst. Org. Chem., Univ. Ljubljana, Murnikova, Yugoslavia). *Z. anal. Chem.*, 1956, **151** (3), 187–191.—4-*p*-Bromophenylthiosemicarbazide (**I**) is preferred to 4-phenyl- and 4-*p*-tolylthiosemicarbazides (*cf. Anal. Abstr.*, 1956, **3**, 2118; 2766) and semicarbazide as a reagent for the characterisation of aldehydes and ketones. Details for the preparation of **I** are given, and lists of melting points of the 4-*p*-bromophenylthiosemicarbazones of 33 aldehydes and 11 ketones. *Procedure*—Reflux the carbonyl compound (0·0025 mole) with a soln. of **I** (0·0025 mole) in 96 per cent. ethanol (20 to 25 ml) on a water bath for 5 or 10 min. (or 30 min. for benzylideneacetone), cool, concentrate by evaporation if crystals do not form, filter and recrystallise from ethanol or dioxan. A. R. ROGERS

3080. **Partition chromatography of aliphatic acids. Quantitative resolution of normal-chain even acids from C_{12} to C_{24}.** F. A. Vandenheuvel and D. R. Vatcher (Fisheries Res. Board, Halifax, Nova Scotia, Canada). *Anal. Chem.*, 1956, **28** (5), 838–845.—Quantitative resolution of mixtures of even-numbered, normal-chain saturated C_{12} to C_{24} fatty acids is obtained by reversed-phase chromatography on a silane-treated silicic acid column with 2:2:4-trimethylpentane (*iso*octane) as the stationary phase and aq. methanol as the eluting solvent. The eluate flows into a receiving flask to which are added successive increments of standard alkali, and the time required for the neutralisation of each increment is noted. The peak positions of the various acids eluted are determined from these data. Less than 50 mg of mixed acids are needed and components representing > 10 per cent. of the mixture are determined with an error < 2·5 per cent. A comparable degree of accuracy for minor components (1 to 3 per cent.) is attained when a procedure involving a complementary analysis is followed. G. P. COOK

3081. **Paper chromatography of fatty acids and halogenated organic acids.** M. H. Hashmi and C. F. Cullis (Imp. Coll. Sci. and Technol., London). *Anal. Chim. Acta*, 1956, **14** (4), 336–338.—The method described is suitable for the separation and analysis of volatile fatty acids and some halogenated organic acids. The acids (50 to 100 μg) are spotted on Whatman No. 4 filter-paper and developed for about 18 hr. with a solvent consisting of *n*-propanol and conc. aq. NH_3 (7:3 by vol.). The acids are identified as follows. *Fatty acids*—Spray with B.D.H. Universal Indicator adjusted to pH 9·5. All the acids appear as red spots on a

blue ground. The halogenated acids are distinguished as follows. *Iodo acids*—The chromatograms are hung in an atmosphere of chlorine for 5 to 10 sec. The acids appear as yellow spots on a white ground. *Bromo acids*—The chromatograms are sprayed with 0·1 per cent. fluorescein soln. in 75 per cent. v/v aq. ethanol, and then hung in a chlorine tank for 5 sec. The acids are revealed as red spots on a white ground. *Mixtures of bromo and iodo acids*—The use of the bromo acid spray reveals the iodo acids as yellow spots on a white ground. C. A. SLATER

3082. **Potentiometric titration of very weak acids. Titration in ethylenediamine solution using platinum electrodes.** G. A. Harlow, C. M. Noble and G. E. A. Wyld (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 784–786.—The use of anodically polarised platinum wire as an indicator electrode for the titration of very weak acids in ethylenediamine yields titration curves over a range of potential 2 to 3 times as great as those obtained with the glass electrode and with greater reproducibility than with the antimony electrode. The reference electrode is a short length of platinum wire inserted into the flow of the titrant (0·2 *N* KOH in *iso*propyl alcohol). The main advantage of the platinum electrode over the glass electrode is the freedom from errors caused by alkali ions. W. J. BAKER

3083. **Potentiometric titration of very weak acids. Tetrabutylammonium hydroxide as titrant in non-aqueous media.** G. A. Harlow, C. M. Noble and G. E. A. Wyld (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 787–791.—The automatic potentiometric titration of very weak acids in non-aq. solvents [ethylenediamine, pyridine (**I**), *iso*propyl alcohol and ethyl methyl ketone (**II**)] can be effected with 0·2 *N* tetrabutylammonium hydroxide in nearly anhyd. *iso*propyl alcohol. Difficulties caused by pptn. are minimised and, owing to the absence of K^+, there is no loss in sensitivity when a glass electrode is used. Titration curves for phenol and a mixture of phenol and acetic acid with HCl, in various solvents, are shown and discussed. The titrant is prepared by passing a soln. of tetrabutylammonium iodide in *iso*propyl alcohol through an anion-exchange column (OH form). The preferred solvents for the sample are **I** and **II**.
W. J. BAKER

3084. **Tetrabutylammonium hydroxide as titrant for acids in non-aqueous solutions.** R. H. Cundiff and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 792–797.—Tetrabutylammonium hydroxide (**I**) in benzene - methanol is a stable titrant yielding constant and reproducible potentials with a glass - calomel or methanol-modified calomel electrode, without formation of any ppt. A 0·1 *N* soln. of **I** (prepared from tetrabutylammonium iodide and standardised against benzoic acid) is used and the titrations are made in an atm. of N when basic solvents, *e.g.*, pyridine, dimethylformamide, are used. The procedure is suitable for the determination of many acidic compounds, *viz*, phenols, amino acids, imides, thiols, enols, mono-, di- and tri-basic acids, amine salts of weak and strong acids, and mixtures of very weak, weak and strong acids. Many of these acidic compounds can be titrated visually, in pyridine, with either thymol blue or azo violet indicator, the soln. of **I** being added as rapidly as possible. In certain solvents, especially pyridine, sharp inflections are obtained potentiometrically for each equivalent of each acid, *e.g.*, oxalic, tartaric, malic, succinic, fumaric, phthalic and sulphuric acids. Typical titration curves for separate acids and for mixtures of acids are shown. The titrant prepared by an ion-exchange process (*cf. Anal. Abstr.*, 1956, **3**, 3083) is regarded as unsuitable. W. J. BAKER

3085. **Spot test for acetate in formic acid and formates.** F. Feigl and C. Stark (Lab. Prod. Mineral, Min. Agric., Rio de Janeiro, Brazil). *Chemist Analyst*, 1956, **45** (2), 46–47.—Acetic acid and acetates in formic acid and formates can be detected with great sensitivity by reduction to acetaldehyde, which forms a blue colour with nitroprusside - morpholine. The procedure is far less sensitive for the detection of lactic, butyric and propionic acids in formic acid. A mixture of one drop of the formic acid is dried with pulverised $CaCO_3$ in a micro test-tube. A filter-paper, moistened with nitroprusside - morpholine, is placed over the mouth of the cooled tube. When the tube is heated a blue stain appears if acetic acid is present. Formates are tested without adding $CaCO_3$. (*Cf. Anal. Abstr.*, 1956, **3**, 3075.) O. M. WHITTON

3086. **The detection of bromoacetic acid.** H. Pfudl (Bundesanstalt für Lebensmitteluntersuchung, Vienna, Austria). *Z. anal. Chem.*, 1956, **151** (3), 191–195.—A method is given for the detection of bromoacetic acid (**I**), used as a preservative in food products. *Procedure*—Saponify the sample, acidify, and extract with ether. Separate the acids by chromatography on paper previously treated with oxalic acid, with ethanol - aq. NH_3 - H_2O (100:7:18) for development. **I** has an R_F value of 0·55, but for certain identification the presence of Br in the acid must be proved.
A. R. ROGERS

3087. **Ultra-violet spectrophotometry of vinyl acetate. II. Determination of acetone and divinylacetylene in vinyl acetate.** C. Capitani, E. Milani and E. Peccatori (Soc. Rhodiatoce, Novara, Italy). *Chim. e Ind.*, 1956, **38**, 102–108.—Of the possible impurities in vinyl acetate, *viz*, acetic acid, ethylidene diacetate, vinylacetylene, acetone and divinylacetylene, only the last two show characteristic ultra-violet absorption in the region in which vinyl acetate is transparent, and procedures have been developed for their determination. Acetone in concentrations of 0·05 to 0·5 per cent. may be determined from measurements of the extinction at the maximum at 275 mμ ($\epsilon = 2{\cdot}5$) and divinylacetylene (which shows exceptionally high absorption) in concentrations of 0·00005 to 0·003 per cent. from measurements at the maximum at 266 mμ ($\epsilon = 1870$). A two-component analysis, where both impurities are present, has been worked out. L. A. O'NEILL

3088. **Detection of carbohydrates on paper chromatograms.** M. L. Wolfrom and J. B. Miller (Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1037.—Carbohydrates and related substances are easily detected on developed paper chromatograms by successively spraying with aq. sodium periodate, aq. $KMnO_4$, water, and an acid soln. of benzidine. By this method, 0·5 μg of mannitol, 2·4 μg of glucose and 7·8 μg of sucrose can be detected. G. P. COOK

3089. **Cerate oxidimetry. IV. Oxidation of carbohydrates.** N. N. Sharma (University of Allahabad, India). *Anal. Chim. Acta*, 1956, **14** (5), 423–426.—Various sugars are boiled with a 100 per cent. excess of $Ce(SO_4)_2$ in dil. H_2SO_4 and the excess of Ce^{IV} is titrated with standard Fe^{II} soln. Glucose is oxidised in 15 min., consuming 6 equiv. of O and yielding formic acid; fructose consumes 7 equiv. of O and yields formic acid and CO_2. Sucrose and lactose each consume 13 equiv. of O and yield formic acid and CO_2. Xylose is oxidised in 10 min. by 5 equiv. of O and yields formic acid. W. C. JOHNSON

3090. **Microscopic identification of microgram quantities of D-mannose and D-lyxose. Direct synthesis of crystalline D-mannose and D-lyxose phenylhydrazones by solvent-diffusion technique.** L. M. White and G. E. Secor (U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1052–1053.—An extension of the solvent-diffusion technique for the identification of D-fructose and L-arabinose (*cf.* White and Secor, *Anal. Chem.*, 1955, **27**, 1016 and 1998) to the microscopic identification of microgram amounts of D-mannose is presented. The reaction of D-mannose with phenylhydrazine is controlled to give the characteristic hydrazone with as little as 1 μg of pure or 10 to 15 μg of chromatographically separated D-mannose. Under the same conditions, 5 to 10 μg of pure and 15 to 25 μg of chromatographed D-lyxose are required for identification of its phenylhydrazone. L-Fucose can be similarly identified but the test is much less sensitive. G. P. COOK

3091. **Determination of hydroxyalkyl groups in low-substituted starch ethers.** H. J. Lortz (Penick & Ford Ltd. Inc., Cedar Rapids, Iowa, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 892–895.—The method is a modification of that of Morgan (*Ind. Eng. Chem., Anal. Ed.*, 1946, **18**, 500). The degree of substitution of low-substituted hydroxyalkyl starch ethers is determined by reaction with hot constant-boiling HI; the hydroxyalkyl groups decompose into ethyl iodide and ethylene, which are absorbed in standard soln. of $AgNO_3$ and Br, respectively. The ethyl iodide and ethylene are determined volumetrically. The average variation between duplicates is 3 per cent. G. P. COOK

3092. **Analysis of currently used chlorinated solvents by infra-red absorption.** A. Berton. *Chim. Anal.*, 1956, **38** (6), 207–211.—The i.r. spectra between 2 and 15 μ of CCl_4, tetra-, tri- and di-chloroethylenes, chloroform, dichloromethane and di- and tetra-chloroethanes are described, and the effect of dilution is discussed. Suitable wavelengths for qual. detection are pointed out and possible interfering bands in other solvents are listed. The possibilities of using the method for quant. determination are discussed and the precision attainable is given. E. J. H. BIRCH

3093. **Absorptiometric study of certain organic fluorine compounds.** F. Kingdon and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 860–864.—Fluorinated 1:3-diones can be applied to the absorptiometric determination of some metal ions over a limited concn. range. A method for the determination of $Fe^{\cdots}$, in which thenoyltrifluoroacetone is used, is described in detail. The error is within $\pm$ 3 per cent.; the method is subject to interference from $\simeq$ 40 radicles and has a relatively low sensitivity. The determination of bromo-, chloro-, 1:3-dichloro- and 1:1:1-trifluoroacetone is also described, the procedure being essentially that of Greenberg and Lester (*J. Biol. Chem.*, 1944, **154**, 177) and involves reaction with 2:4-dinitrophenylhydrazine, with spectrophotometric measurement of the extracted colour. G. P. COOK

3094. **Qualitative and semi-quantitative tests for amine hydrochlorides on paper chromatograms.** S. D. Nogare (E. I. du Pont de Nemours & Co. Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 903.—The tests described are based on the reaction of Cl' with Ag^+. Qualitatively, the amine hydrochloride spots are detected by the reduction of AgCl to metallic Ag. Spots containing as little as 3 μg of Cl' can be detected. Semi-quantitatively, the chloride content of the spots from a separate chromatogram is titrated by a sensitive potentiometric procedure. An average recovery of 88 per cent. with a standard deviation of $\simeq \pm$ 8 per cent. was obtained with pyrrolidine - ethylenediamine mixtures containing $\simeq$ 50 to 500 μg of pyrrolidine. G. P. COOK

3095. **Separation and detection of cyanamide and its derivatives and determination of urea by paper chromatography.** J. E. Milks and R. H. Janes (N. Amer. Cyanamid Ltd., Welland Plant, Niagara Falls, Ontario, Canada). *Anal. Chem.*, 1956, **28** (5), 846–849.—Cyanamide and its derivatives which are formed in the manufacture of dicyandiamide were chromatographed with *n*-butanol - ethanol - water (4:1:1) and with ethyl methyl ketone - light petroleum - water (9:4:3) on filter-paper. Sixteen spots were detected and cyanourea, biguanide, melamine, three salts of guanidine, urea, guanylthiourea, thiocyanate, thiourea, dicyandiamide and cyanamide were characterised. Urea was determined spectrophotometrically on the water extract of the urea spots. Recovery was 95 per cent. G. P. COOK

3096. **Polarography of some purine derivatives.** N. G. Luthy and B. Lamb (Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1956, **8** (6), 410–416.—A quantitative study has been made of the reduction waves obtained by polarography of acetyladenine in a soln. of perchloric acid of various concn. in 50 per cent. aq. ethanol. The ethanol in the solvent prevents rapid hydrolysis to adenine, which has only one reduction wave. Possible applications in biological research are mentioned. A. R. ROGERS

3097. **New colour test for thiols and thiol esters.** R. Benesch, R. E. Benesch, M. Gutcho and L. Laufer (Inst. for Enzyme Research, Univ. of Wisconsin, Madison, U.S.A.). *Science*, 1956, **123**, 981–982.—When the products of the reaction between N-ethylmaleimide (**I**) and thiols are made alkaline, a red colour develops. A sensitive test for thiols and thiol esters based on this observation is recommended, especially for detecting these compounds in paper chromatograms. After drying the paper thoroughly in a current of air, it is dipped in a 0·05 *M* soln. of **I** in absolute *iso*propyl alcohol, again dried in a current of air for 15 min. and then dipped in 0·25 *M* KOH in absolute *iso*propyl alcohol. Pink to red spots appear immediately. The colour test was used successfully after chromatography with the following solvent systems—*iso*propyl alcohol - formic acid - water, *n*-propanol -

water, *n*-butanol - formic acid - water, *iso*propyl alcohol - ethanol - formic acid - water. As little as 1 μg of glutathione or 0·1 μg of sulphydryl could be detected but the colour faded after a few hr. Higher amounts, 3 μg or above, were stable for more than 48 hr. A no. of compounds giving a positive or negative reaction to the test are listed.
H. F. W. KIRKPATRICK

3098. **Use of iodine chloride in analytical chemistry. IV. The determination of thiourea.** J. Čihalík and J. Růžička (Karlova Univ., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (1), 262–264.—Thiourea is oxidised by iodine chloride in neutral to strongly acid solution (up to 6 *N* HCl) to $[(NH)(NH_2)CS]_2$. A good potentiometric end-point (platinum and S.C.E.) is obtained in 0·004 *M* solutions, but 0·0002 *M* solutions can be titrated. The reaction is not stoicheiometric in alkaline solution. P. S. STROSS

3099. **Estimation of micro quantities of thiocholine esters.** E. Heilbronn (Res. Inst. of Nat. Defence, Sundbyberg, Sweden). *Acta Chem. Scand.*, 1956, **10** (2), 337–338.—The method developed by Hestrin for the estimation of choline esters and other carboxylic acid derivatives (*J. Biol. Chem.*, 1949, **180**, 249) is shown to be applicable to the thiocholine esters. The method is based on the reaction (in alkaline solution)—

$$R{\cdot}COOR' + H_2NOH \rightarrow R{\cdot}CO{\cdot}NHOH + R'OH.$$

The resulting hydroxamic acid is determined colorimetrically as its ferric complex, which has an absorption max. at 510 mμ. C. A. SLATER

3100. **Infra-red absorption spectra of disubstituted naphthalenes.** Hitoshi Kamada and Shigeyuki Tanaka (Inst. of Techno-Anal. Chem., Faculty of Eng., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1956, **5** (2), 98–101.—The i.r. absorption spectra of a variety of disubstituted naphthalenes (47 samples) were measured with a Baird double-beam spectrometer, and their use for qualitative and quantitative analysis was examined. The 1:2-, 1:4-, 1:5-, 1:7-, 2:3-, 2:6- and 2:7-substituted naphthalene derivatives each shows characteristic absorption at a definite wavelength between 11 and 14 μ. Compounds substituted in positions 2:6 and 2:7 having a sulphonic acid group in either or both positions also show a strong absorption at 9·1 ± 0·02 μ. K. SAITO

3101. **The estimation of catechol in commercial catechol fractions by infra-red spectrophotometry.** O. Kunc and L. Sokol. *Chem. Průmysl*, 1956, **6** (1), 31.—The base-line method, which enables the substantial elimination of absorption from materials other than the one under examination, was used. Calibration of the Perkin - Elmer instrument (model 12B) used was by means of 0·07 to 0·09 g of pure catechol in 5 ml of acetone soln. The analyses were carried out on samples of 0·2 to 0·35 g in 5 ml of acetone. The spectrum was observed between 700 and 780 cm^{-1}. The use of the linear relationship between concn. and extinction was confirmed and used to calculate the results, which were accurate to within ± 1·7 per cent. A. O. JAKUBOVIC

3102. **Chromatographic separation of some aromatic nitrogen compounds.** W. R. Edwards, jun., O. S. Pascual and C. W. Tate (La. State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1045–1046.—Chromatographic data for over 30 nitrogen compounds are listed and spectrophotometric data for 17 of these compounds are included. Recoveries ranged from 96 to 99 per cent. under the conditions most favourable for each individual compound. This work is an extension of that by Edwards and Tate (*Anal. Chem.*, 1951, **23**, 826). G. P. COOK

3103. **Analysis of xylidine fraction by use of infra-red absorption spectra.** Shigeyuki Tanaka, Hisakazu Arakawa and Koji Yoshimura (Kawasaki Iron Works, Nihon Kokan Co., Kawasaki). *Japan Analyst*, 1956, **5** (3), 145–149.—The determination of six isomers of xylidine in a coal-tar fraction (boiling range 205° to 230° C) was studied by the use of a Baird i.r. spectrophotometer (key bands, 12·11 μ for the 3:5-isomer; 12·35 for 2:4-; 12·39 and 11·72 for 3:4-; 12·57 for 2:5-; 12·97 for 2:3-; and 13·14 for 2:6-). The xylidine fraction contains ≃ 3 per cent. of other ingredients, mainly phenol and tertiary amines. The phenol is removed by extraction with ether from an acid soln.; the amines are treated with acetic anhydride and the acetyl compound is fractionally distilled, the fraction at 160° to 240° C being collected. The purified xylidines are dissolved in benzene to produce a 10 per cent. soln. and submitted to i.r. spectrophotometry. The standard deviation is ≃ 1·5 per cent. for the 3:5-, 2:5-, 2:3- and 2:6-isomers, and ≃ 2 per cent. for the 3:4- and 2:4-isomers.
K. SAITO

3104. **An assay for primary arylalkylamines.** A. McCoubrey (Maudsley Hospital, London, S.E.5, England). *J. Pharm. Pharmacol.*, 1956, **8** (6), 442–446.—A colorimetric method is given for the assay of primary arylalkylamines, based on the formation of the substituted salicylaldimine. Recoveries range from 80 to 100 per cent. Glycine, NH_3, acetone, ethyl acetoacetate, secondary and tertiary amines, primary amines of low molecular weight and arylamines do not interfere. Human urine gave small positive readings. *Procedure*—Acidify the soln. and remove CO_2 by a stream of N at 40° C. Adjust to pH 9 and extract with benzene (or other volatile solvent) (5 × 5 ml). Mix with a benzene soln. of salicylaldehyde (≃ 10 equiv.) and concentrate to small bulk in a stream of air on a sand bath. Dilute to 20 ml and mix a 5-ml aliquot with 1 per cent. acetic acid in benzene (0·5 ml). Remove the solvent in a stream of air and remove excess of salicylaldehyde by distillation at 70° C and 0·5 mm pressure for 30 min. Dissolve the residue in warm ethanol (5 ml). Add *N* aq. NaOH (1 ml) and H_2O (4 ml) and measure the extinction at 415 mμ. Submit a blank and a suitable amount of pure aldimine to the same procedure. Slight modifications to the procedure are required with certain amines. At low concn. (< 10 μg per ml salicylaldehyde equivalent), fluorimetry may replace colorimetry. Mescaline and amphetamine may be determined by this method. A. R. ROGERS

3105. **Voltammetry at solid electrodes. Anodic polarography of the phenylenediamines.** R. E. Parker and R. N. Adams (Princeton Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 828–832.—Results are reported for the anodic polarography of the *o*- and *p*-phenylenediamines at a rotating platinum electrode, with a current-scanning technique (*Ibid.*, 1953, **25**, 1160). Values of pK_a (acidic dissociation const.) of reduced and

oxidised species were calculated from the observed variation of $E_{\frac{1}{4}}$ with pH. In all instances a linear plot of limiting current *vs.* concn. was obtained. Quant. determinations of *o*- or *p*-phenylenediamine at concn. of 10^{-5} to 10^{-4} *M* can be made, with a reproducibility of 2 to 3 per cent., by measuring limiting currents at the rotated platinum electrode. The results of analyses of mixtures of the two diamines are generally only semi-quant.

W. J. BAKER

3106. **Polarographic behaviour of benzaldehyde derivatives of hydrazine, 1:1-dimethylhydrazine and monomethylhydrazine.** G. C. Whitnack, J. E. Young, H. H. Sisler and E. St. Clair Gantz (U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 833–836.—A study of the polarographic behaviour of benzalazine (**I**), benzaldehydedimethylhydrazone (**II**) and tribenzylidene bismethylhydrazine $[(C_6H_5CH{:}N{\cdot}NCH_3)_2CHC_6H_5]$ (**III**) is presented. In an ethanolic soln. containing quaternary ammonium salts as supporting electrolytes, well-defined diffusion currents, proportional to the concn. in the range 1 to 3 m*M*, were produced over the pH range 3 to 12. Admixtures of **I** and **II** were best determined by using a 75 per cent. ethanol soln. which was $\simeq$ 0·12 *M* in tetra-*n*-butylammonium hydroxide and 0·1 *M* in H_3PO_4; recoveries of **I** were $>$ 97 per cent. and of **II** were $>$ 96 per cent. Soln. of **III** hydrolysed to benzaldehyde too rapidly for precise determination.

G. P. COOK

3107. **Revised method, IP 71T, for the determination of kinematic viscosity in CGS units.** Inst. Petroleum, B.S.I. and A.S.T.M. *J. Inst. Petrol.*, 1955, **41**, 326–327.—The revised Institute of Petroleum method, IP 71T, for measuring, by means of glass capillary-type viscometers, the kinematic viscosity of oils that flow in a Newtonian manner under the conditions of the test, is summarised. The method is applicable to transparent and opaque oils over the temperature range −65° F to +212° F. The viscosity of freshly distilled water (0·01002 poise at 20·00° C) is taken as standard; secondary calibrating liquids are used to standardise viscometers for oil measurements. Various viscometers are described in the appendices, with information on master, or calibrating, viscometers. Also appended are details of *B* (the coefficient of kinetic energy), and values for the minimum flow time, with methods of calculation. The original specification must be consulted for full details. E. G. CUMMINS

3108. **The characterisation of paraffins.** A. Mutschin and C. Glassmann (Fa. Zschimmer and Schwarz A.-G., Oberlahnstein, Germany). *Z. anal. Chem.*, 1956, **151** (3), 161–169.—The i.r. spectra and the appearance in polarised light of crystals of the unsulphonated portion of paraffins can be used for their characterisation. A. R. ROGERS

3109. **Qualitative test for TEL [tetraethyl-lead] in gasoline.** G. E. Mapstone (South African Torbanite Mining and Refining Co. Ltd.). *J. Inst. Petrol.*, 1956, **42**, 67.—To 10 ml of gasoline are added 5 to 10 drops of 2 per cent. I (in ethanol) and the mixture is exposed to u.v. radiation for 5 to 10 min.; 1 ml of solution containing 200 g of NaOH and 50 g of Na_2S per litre is added and the mixture is agitated to remove the colour of the I. The presence of TEL is indicated by the formation of a black film of PbS at the liquid interface.

S.C.I. ABSTR.

3110. **Detection and determination of contamination of aviation gasoline by heavier fuels.** J. A. Krynitsky and W. D. Garrett (Naval Res. Lab., Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 967–971.—The method involves the suspension of the lower portion of a strip of filter-paper in the petroleum and the passing of an air stream over the exposed paper surface. The petroleum rises up the paper by capillary action and is evaporated; the height to which the paper is wetted in a given time (creep height) is governed by the quantity and volatility of the heavy components of the petroleum. The effect of the heavier fuel generally is to increase the creep height. The response is semi-logarithmic, and more sensitive results are therefore given at the lower levels of 0 to 1 per cent. of contamination. G. P. COOK

3111. **The spectrographic analysis of lubricating oils.** D. L. Fry (General Motors Corp., Detroit, Mich., U.S.A.). *Applied Spectroscopy*, 1956, **10** (2), 65–68.—Improvements in the rotating-disc method were effected by using a lithium naphthenate buffer equivalent to 0·15 per cent. of Li. This reduced matrix effects to negligible proportions and improved line-to-background intensity ratios. The use of a copper shaft is recommended with arc-like sources to prevent overheating and igniting of the sample. Cobalt was added as an internal standard. Comparisons of the sensitivities of various methods are shown and the advantages and disadvantages of each are discussed.

P. T. BEALE

3112. **Simple method for the identification of paraffin wax in wax mixtures.** W. Hessler (Werner u. Mertz A.-G., Mainz, Germany). *Fette u. Seifen*, 1956, **58** (1), 1–3.—When a cooled slab of wax containing an admixture of paraffin wax is brought into contact with saturated urea solution, a chalky outgrowth appears on the wax surface. For the detection of paraffin wax, a sample of the melted wax is poured into a metal tube, 30 mm high and 25 mm inside diameter, placed on a glass plate, to form a disc 10 mm thick. The tube is placed in a refrigerator for 1 hr. and the wax disc is removed. One drop of conc. urea solution is placed on the smooth side of the disc, which is then allowed to dry completely. The crystals of urea are carefully washed off with water and the disc is allowed to dry again; the appearance of chalky outgrowths indicates the presence of paraffin wax. With most waxes it is possible to detect as little as 1 per cent. of paraffin wax; with hard waxes the limit is 3 to 5 per cent. E. HAYES

3113. **Simplified rapid methods for determining the softening point of resins and bitumens.** K. M. Oesterle. *Schweiz. Arch. angew. Wiss.*, 1956, **22**, 1–9.—The need for methods quicker than the present recognised softening-point tests is discussed. Two procedures are described—(*i*) the ball infiltration method in which the temp. is taken at which the ball sinks, under its own weight, half-way into the test material; (*ii*) the needle zero-pressure method, in which the needle is heated until it just penetrates into the test material, as indicated by a deflection of a balance on which the latter is placed. This method is preferred, and its advantages, *e.g.*, avoidance of the necessity for any alteration of physical form of the test material, are discussed. A definition of softening point is suggested, being that temp. at which an infinitely thin needle under an infinitely small pressure

penetrates the resin surface to an infinitely small extent; this is obtainable on the apparatus described by extrapolation of test results to zero pressure, although for technical reasons a single reading suffices. Comparison is given of results on various materials (including bitumens) by different procedures (K–S, R and B, capillary tube, hot table and needle zero-pressure).

J. Inst. Petroleum Abstr.

3114. **Chromatographic method for the separation of bitumen into its different constituents.** —.Temme. *Bitumen, Teere, Asphalte, Peche*, 1956, **7** (2), 46–49.—An aluminium disc is coated with 5 g of bitumen and extracted with *n*-pentane. The disc is washed clean, and the insoluble asphaltenes are filtered off on asbestos, washed, dried at 105° C and weighed. The filtrate is concentrated to 50 ml and added to a column of fuller's earth (15 times the weight of dissolved bitumen) packed in *n*-pentane. Elution with *n*-pentane and evaporation of the eluate to dryness by irradiation from a 250-watt lamp, followed by 15 min. at 105° C, gives the pale oil fraction. Subsequent elutions with dichloromethane, ethyl methyl ketone and 90 per cent. acetone followed by chloroform give respectively, the dark oil, asphalt resin and acetone - chloroform soluble fractions. The method is rapid and gives reproducible results. A. B. Densham

3115. **Determination of cotton in mixtures with viscose rayon by means of sulphuric acid.** E. Druce (Brit. Cotton Ind. Res. Assoc., Didsbury, Manchester, England). *Shirley Inst. Mem.*, 1956, **29** (7), 57–65.—The method of Howlett, Morley and Urquhart (*Shirley Inst. Mem.*, 1941–43, **18**, 153), for determining cotton in mixtures with viscose rayon by dissolving out the rayon in 60 per cent. H_2SO_4 and weighing the residue, has been re-examined for possible sources of error. Complete dissolution of highly twisted spun viscose rayon is achieved if the yarns are first shaken in water in an end-to-end shaker and dried. The optimum concn. of H_2SO_4 is shown to be 59 $\pm$ 0·25 per cent., and a treatment time of $\frac{1}{2}$ to 2 hr., temp. of 15° to 25°C, and sample wt. of 0·25 to 0·75 g are found to be satisfactory. Corrections are given for the loss of non-cellulosic material in raw cotton yarn, sized yarn or loom-state cloth, scoured cloth and bleached cloth. A modified procedure, which has been found to give results correct within $\pm$ 0·6 per cent., is described. A. M. Spratt

3116. **The determination of sulphur and its compounds in rayon.** M. J. Maurice (N. V. Onderzoekingsinst. "Research"), 1956, 101 pp.—This academic thesis is a critical review of the available methods and includes among the experimental procedures some new methods. From tests to compare their accuracy, a scheme was developed for the determination of all the types of S-containing compounds. It was found that SO_4'' were present mainly as $NaHSO_4$ and that SO_3'' were also present. The reductions were carried out by using the reducing mixture (**I**) of Pepkowitz and Shirley (*Anal. Chem.*, 1951, **23**, 1709). The suggested scheme of analysis is as follows. Sulphide is destroyed with 6 *N* HCl, and the H_2S that is evolved is absorbed in 0·02 *N* Cu^{++} acetate soln. The excess of Cu^{++} is back-titrated with 0·01 *N* EDTA soln. in the presence of murexide, tartaric acid and aq. NH_3. Xanthate is determined by destruction with 6 *N* HCl; the CS_2 is distilled out and is absorbed in ethanolic KOH and the K ethylxanthate is determined either spectrophotometrically at 301 mμ, or potentiometrically with Cu^{++} acetate. Elementary S is extracted with *n*-hexane and is either determined spectrophotometrically at 276 mμ, or else it is reduced with **I** and the H_2S determined as before. When finish is present, dry ethanol is used for extraction (this is rather slow) and the S is determined as H_2S. Sulphate as Na_2SO_4 is fumed with HCl, ignited and reduced with **I** to H_2S, which is determined as described above. Total SO_4'' is found similarly, after treatment with NaOH. Sulphite is destroyed with 4 *N* H_2SO_4, the SO_2 which is formed is absorbed in slightly acidic H_2O_2 and the H_2SO_4 formed is titrated with NaOH every 5 min. during the absorption. Sulphur, sulphide and SO_4'' are found by reduction with **I** and determination of the H_2S. The total sulphur is obtained by oxidising the yarn in a nickel-plated Parr bomb by means of Na_2O_2 and determining the SO_4'' as already described. The main sources of error are the reduction to H_2S, the evolution of H_2S from the hot acid soln. and the NaOH treatment of the yarn to prevent loss of HSO_4', but generally the total content of sulphur as calculated from the individual determinations did not differ significantly from the value obtained directly. (61 references.) A. G. Peto

3117. **An electronic moisture meter for jute: its design and construction.** B. L. Banerjee and M. K. Sen (Indian Jute Mills Assoc. Res. Inst., Calcutta). *J. Sci. Ind. Res., A, India*, 1956, **15** (1), 24-28.—The moisture meter described can be used for testing bales and loose jute. Its principle is based on the variation in the electrical resistance of fibres. The error of measurement is $\pm$ 0·5 per cent. in the low and medium ranges. In the high range, the error varies from + 1 to $\pm$ 5 per cent. with increase in the scale reading. The instrument is robust and durable, does not require frequent battery replacement, and is cheaper than the commercial models available. O. M. Whitton

3118. **Paper-chromatographic analysis of aldehydes and ketones. III. Quantitative determination of aldehydes and ketones in essential oils and perfume compositions.** K. E. Schulte and C. B. Storp (Pharm. Inst. der Freien Univ., Berlin). *Fette u. Seifen*, 1956, **58** (1), 35–39.—Methods developed for the analysis of pure aldehydes and ketones (*Anal. Abstr.*, 1956, **3**, 1395) are applied to the determination of important constituents in essential oils and perfume compositions. The following are determined by chromatography on S. & S. 2043b paper—(*i*) citral in oil of lemon, (*ii*) cinnamaldehyde in cinnamon oil, (*iii*) methyl nonyl ketone in oil of rue, (*iv*) irone in oil of orris, (*v*) ionone in a violet perfume composition and (*vi*) undec- and dodec-aldehydes in a crêpe de Chine perfume composition. Methanol - acetic acid (9·25 : 0·75) is used as the mobile phase for (*i*), (*ii*), (*iii*) and (*vi*), methanol - acetone (6 : 4) for (*iv*), and methanol - acetone (8 : 2) for (*v*). Anisaldehyde and *p*-methylphenylacetaldehyde could not be clearly separated from a lilac perfume composition. E. Hayes

3119. **Use of ionic dyes in the analysis of ionic surfactants and other ionic organic compounds.** P. Mukerjee (Univ. S. Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 870–873.—The method is based on the interaction between ionic dyes and ionic surfactants of opposite charge, extraction of

the reaction product into an organic solvent and measurement of the extinction at a suitable wavelength. The concn. range is 0·1 to 1 p.p.m. and the limit of detection is $\simeq$ 0·002 p.p.m.

G. P. Cook

3120. **Polarographic determination of methyl methacrylate monomer in polymers.** R. J. Lacoste, I. Rosenthal and C. H. Schmittinger (Rohm & Haas Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 983–985.—The method is based on the reduction of the $\alpha\beta$-unsaturation of methyl methacrylate. The reduction is applied in a benzene - ethanol - water solvent-system with a tetra-alkylammonium salt as the supporting electrolyte. The methyl methacrylate wave appears at a $E_{\frac{1}{2}}$ of $\simeq$ −2·06 V *vs.* the S.C.E., with 0·1 *N* tetrabutylammonium chloride as the electrolyte. Amounts of monomer, as little as 0·1 per cent. of the polymer, were determined with a precision within $\pm$ 3·0 per cent. G. P. Cook

3121. **Colorimetric determination of bisphenol-type epoxy resins and their fatty acid esters.** M. H. Swann and G. G. Esposito (Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1006–1007.—A modified Marquis reagent develops with bisphenol-type epoxy resins a blue colour which is specific and can be used for quant. measurement of the resins in their unmodified form, in esters and in silicone blends. Since the intensity of colour developed is independent of the mol. wt. of the resin, analysis can be made without knowledge of the polymer length involved. The colour is due to the etherified bisphenol grouping. Recoveries of > 95 per cent. were obtained from epoxy esters of known composition.

G. P. Cook

3122. **Radiotracer studies of analytical methods for styrenated oil-acids and esters.** E. G. Bobalek, J. R. Bradford, F. Leutner and R. Akiyama (Case Inst. Technol., Cleveland, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 906–908.—The Armitage and Kut procedure for the separation and determination of the neutral polystyrene and the copolymer of oil acid and styrene in styrenated paint vehicles (*Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1952, **333**, 671; *Paint Varn. Prod. Mgr*, 1953, **43**, 33) was investigated with radiotracer techniques in polymers prepared from styrene labelled with ^{14}C in the α-carbon position. The procedure, which depends on the differential solubility of the copolymer's calcium soaps and the neutral polystyrene in wet ethyl acetate, was often found to be unreliable owing to the solubility of the copolymer being affected by unknown variables in its composition. G. P. Cook

3123. **Analytical chemistry related to urea resins. I. Quantitative determination of hexamine in an initial reaction product by the use of infra-red absorption spectra.** Shigeyuki Tanaka, Yasuo Miyamoto and Naoki Yoshimi (Inst. of Techno-Anal. Chem., Faculty of Eng., Tokyo Univ., Hongo, Tokyo). *Japan Analyst*, 1956, **5** (2), 87–90.—Since hexamine (**I**) vitiates the i.r. spectroscopic determination of mono- and di(hydroxylmethyl)-urea in the reaction mixture at an early stage in the prep. of urea resins, its removal was studied by the use of various organic solvents. A quant. separation of **I** is effected by a repeated (> 6 times) extraction of the basic reaction mixture with chloroform containing a small amount of methanol. The $CHCl_3$ soln. is diluted with twice its weight of CS_2 and submitted to i.r. spectrophotometry, the key band 8·12 μ being used. The extinction is proportional to the concn. of **I** (< 40 mg per 5 ml). From the results it was found that **I** remains unchanged in the reaction mixture during the initial stage of polymerisation.

K. Saito

3124. **Chromatographic acid-hydrolysis method for determination of triacetin in double-base powder.** J. O. Watts and H. Stalcup (U.S. Naval Powder Factory, Indian Head, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 975–978.—The triacetin is extracted from double-base powder (a powder containing both nitroglycerin and cellulose nitrate) into dichloromethane and is separated from nitroglycerin and other components by chromatography on a silicic acid - Celite column. The triacetin, after elution, is hydrolysed with HCl and the liberated acetic acid is determined by titration with standard alkali. Recoveries of 99·1 per cent. were obtained from synthetic samples in the absence of nitroglycerin; in the presence of nitroglycerin, recoveries averaged 99·54 per cent.

G. P. Cook

See also Abstracts 3172, 3173, 3200, 3221, 3231.

4.—BIOCHEMISTRY
INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

3125. **Inorganic constituents in biological materials. VII. Simultaneous spectrochemical analysis of inorganic constituents with a step-sector disc.** Naoichi Ohta and Yasuo Tomita (Faculty of Sci., Tokyo Metropolitan Univ., Setagaya-ku, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (3), 454–458.—The spectrographic determination of Ca, Sr, Ba, Mg, Na and K with a step sector was applied to the analysis of traces of metals in organs of mammals. The intensity of lines of suitable strength was compared with that of Ni as the internal standard (3002·49 A for Na and Mg; 3858·3 A for others). The range of quant. analysis was thus increased sufficiently for K ($\simeq$ 3 mg per g of wet organ) and Ca ($\simeq$ 0·03 mg per g) to be simultaneously determined.

K. Saito

3126. **A preliminary communication on a conductimetric screening test for electrolytes [in plasma].** E. Boesen and P. A. Loud (Central Lab., Portsmouth, England). *J. Clin. Pathol.*, 1956, **9** (2), 173–175.—It is suggested that determination of the electroconductivity of plasma and thence calculating the total electrolytes would eliminate a large proportion of cases with normal electrolytic balance from the necessity of a more detailed analysis. A suitable method is described.

H. F. W. Kirkpatrick

3127. **Assay of tritium activity in body fluids with use of a liquid scintillation system.** W. H. Langham, W. J. Eversole, F. N. Hayes and T. T. Trujillo (California Univ., Los Alamos, N.M., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47**, (5), 819–825.—Methods are described for the determination of tritium water (H^3HO) in human and rat serum and urine where H^3HO is used as a tracer for ordinary

water in studies of fluid balance and of water metabolism and transfer. Preliminary removal of proteins and pigments was found to be necessary to obtain reproducible results and methods of treatment with trichloroacetic acid or activated charcoal are described. Details are given for the preparation of the scintillation solution for use with a fast coincidence liquid scintillation counter. The recovery or H^3HO is shown to be between 96 and > 99 per cent., with errors of 3 and < 2 per cent., respectively, according to the level of activity. Results obtained in a study of the H^3HO levels in normal human urine and serum after the ingestion of H^3HO are given. W. H. C. SHAW

3128. **Biochemical studies on trace elements. II. The content of beryllium in organs of several mammals.** Tatuo Suzuki and Iwao Hamada (Dept. of Chem., Faculty of Fisheries, Mie Prefectural Univ., Tsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 125–128.—The determination of a micro amount (< 1 μg) of Be in organs was studied by the use of morin (*cf.* Klemperer *et al.*, *Anal. Chem.*, 1950, **22**, 828). When the sample (10 g of dried organ) is decomposed with H_2SO_4 (2 ml) and HNO_3 and co-pptd. with aluminium phosphate, the recovery of Be is ≃ 90 per cent. The content of Be varies with different organs, but is usually ≃ 10^{-3} p.p.m. K. SAITO

3129. **The estimation of magnesium in serum using Titan yellow.** D. W. Neill and R. A. Neely (Royal Victoria Hosp., Belfast). *J. Clin. Pathol.*, 1956, **9** (2), 162–163.—To 1 ml of serum add 5 ml of water, 2 ml of 10 per cent. sodium tungstate and 2 ml of 0·67 *N* H_2SO_4, mix and centrifuge at 2500 r.p.m. for 5 min. To 5 ml of supernatant add 1 ml of water, 1 ml of 0·1 per cent. gum ghatti soln., 1 ml of 0·05 per cent. aq. soln. of Titan yellow, and 2 ml of 4 *N* NaOH. Measure the red colour at 535 mμ. Prepare (*i*) a blank, with 1 ml of $CaCl_2$ soln. (containing 0·05 mg of Ca) (**I**) in place of serum; (*ii*) a standard, by treating 5 ml of soln. containing 12·5 μg of Mg as in the test and adding 1 ml of **I** in place of water; and (*iii*) a standard blank with 5 ml of water and 1 ml of **I**. The addition of Ca to the blanks and standard compensates for the intensification of the colour of the lake by the Ca in serum. By this method, normal values for serum ranged from 1·9 to 2·7 mg of Mg per 100 ml. H. F. W. KIRKPATRICK

3130. **Complexiметric estimation of calcium in serum.** P. H. Schulitz (General Hospital, Barmbek, Hamburg, Germany). *Hoppe-Seyl. Z.*, 1956, **303** (3–6), 257–261.—Calcium is estimated in serum by pptn. with oxalate, followed by the removal of the excess of the oxalate with a bromide - bromate mixture, and subsequent titration with EDTA (disodium salt). *Procedure*—To 1 ml of serum are added 2·5 ml of a pptg. reagent (40 ml of 30 per cent. Na acetate soln. in 30 ml of water and 20 ml of 4 per cent. ammonium oxalate soln.). The mixture is allowed to stand for 4 hr., when 0·5 ml of a Sterox - water mixture (1:50) is added and the whole is centrifuged. The clear filtrate is treated with 0·5 ml of a bromide soln. (4 g of KBr in 100 ml of 2 *N* H_2SO_4) and five drops of $KBrO_3$ soln. (5 per cent.) and heated on a water bath for 15 min. After being cooled, the soln. is treated with 2·5 ml of an ammonia soln. (20 ml of aq. NH_3 soln., 30 ml of water and 50 ml of 90 per cent. ethanol), followed by 0·5 ml of indicator soln. [0·01 g of methyl red, 0·1 g of diamine green and 0·2 g of cresolphthalein complex (Ciba) in 1 ml of water, made up to 10 ml with 90 per cent. ethanol, to which soln. are added a further 9 ml of water and 0·2 ml of a 20 per cent. Na_2CO_3 soln.], and titrated until colourless with 0·001 *M* EDTA (disodium salt). G. R. WHALLEY

3131. **Micro-determination of calcium and magnesium in tissue ashes.** R. L. Griswold and N. Pace (Univ. of California, Berkeley, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1035–1037.—A procedure for separating micro-mole amounts of Ca and Mg from each other and from PO_4''', *e.g.*, in biological tissues, is described. The ashed sample is dissolved in H_2O and diluted to 50 ml. A 10-ml aliquot is passed through a cation-exchange column (10 cm × 0·5 cm, 200 to 400-mesh Dowex 50, H form) at a rate of ≃ 4 ml per hr., after which PO_4''', Mg^{++} and Ca^{++} are eluted separately with *N* HCl (for PO_4''' only) and 3 *N* HCl. The soln. (4 to 8 ml) containing Ca and Mg are evaporated to dryness (100° to 105° C), the residues are redissolved in H_2O and each soln. is then titrated with EDTA (disodium salt) at pH 10·5, with Eriochrome black T as indicator. In the titration for Ca, ≃ 0·025 ml of standard Mg soln. is added and its titre is afterwards subtracted from the final titre (moles); the sharp end-point is thus due to Mg only. Recoveries are ≃ 100 per cent. for Ca and ≃ 97 per cent. for Mg, with deviations < 5 per cent. W. J. BAKER

3132. **Determination of zinc in serum.** J. Rechenberger (Med. Klin. Univ. Leipzig, Germany). *Z. ges. inn. Med.*, 1955, **10**, 645–647.—The micro-method described depends on splitting the Zn^{++} from the blood proteins with 6 *N* HCl and 20 per cent. trichloroacetic acid, conversion of the Zn into Zn dithizonate, and colorimetric estimation of the red substance produced, with filter S53. The method was applied to the serum of 80 normal persons and gave a mean value for the Zn content of 145 μg per cent. with range 115 to 185. No age or sex difference was found.

NUTRITION ABSTR. AND REV.

3133. **Organic mercurial diuretics. I. Polarographic determination of mercury in urine.** Hirokazu Kadowaki, Kihachiro Okamoto and Minoru Nakajima (Kyoto Yakuhin Ind. Ltd., Nishinokyotsukinowa, Kyoto). *J. Pharm. Soc. Japan*, 1955, **75** (5), 485–489.—The polarographic behaviour of a mercurial diuretic, the sodium salt of pyridine-2:3-dicarboxylic acid hydroxymercuryallylamide, was studied in water and in normal urine. The shape of the wave changes with change in pH, but the $E_{\frac{1}{2}}$ value remains constant at pH 3 to 6 and 8 to 10. The polarographic determination (< 10 mg per 100 ml) can be effected at pH 8·4 in the presence of tetramethylammonium bromide and Na_2SO_4. For the determination of total Hg in urine, the sample (20 ml) is decomposed with HNO_3 (8 ml) and H_2SO_4 (1 ml), diluted with water, partly neutralised with 20 per cent. NaOH (2 ml), and submitted to polarography by the usual method. K. SAITO

3134. **An apparatus for micro-determination of carbon dioxide in plasma.** F. Rappaport, F. Eichhorn and M. Nutman (Beilinson Hosp., Petach Tiqua, Israel). *J. Clin. Pathol.*, 1956, **9** (2), 166–170.—A full description is given of an apparatus that enables determination of CO_2 in plasma to be made on 0·05 to 0·1-ml samples with an accuracy

comparable with that of the full-scale Van Slyke apparatus. H. F. W. KIRKPATRICK

3135. **The improved determination of iron in serum.** P. Trinder (Royal Infirmary, Sunderland, Co. Durham, England). *J. Clin. Pathol.*, 1956, **9** (2), 170–172.—To 2 ml of serum in a 15-ml centrifuge tube add 2·5 ml of water and 1·5 ml of 20 per cent. trichloroacetic acid, mix, cover the tube with an aluminium cap and heat for 10 min. in a glass water-bath at 90° to 95° C. Mix the contents of the tube at 5 min. and again just before removal from the bath. Cool, centrifuge briefly, shake the tube to mix the contents and centrifuge at 4000 r.p.m. for 15 min. To 4 ml of clear supernatant and to a blank (3 ml of water and 1 ml of trichloroacetic acid soln. treated as the test) add 0·2 ml of iron reagent, 0·6 ml of 40 per cent. aq. soln. of sodium acetate trihydrate, and 0·4 ml of 50 per cent. v/v H_2SO_4, mixing after each addition. Read the colour at 535 mμ. Prepare a standard graph by treating 3-ml quantities of water containing 0·7 to 5·6 μg of Fe as for the blank. *Iron reagent*—To 100 mg of 4:7-diphenyl-1:10-phenanthroline in a boiling-tube add 0·5 ml of chlorosulphonic acid, boil for 30 sec. over a micro flame, then cool. Cautiously add 10 ml of water, heat in a boiling-water bath until the ppt. dissolves completely. Dilute to 100 ml with water and add 1 ml of thioglycollic acid.

H. F. W. KIRKPATRICK

3136. **Colour test for sugar and blood in urine.** E. Sawicki (Univ. Florida, Gainesville, U.S.A.). *Chemist Analyst*, 1956, **45** (2), 45–46.—Two procedures are described that are sensitive to about 0·003 per cent. of blood or 0·4 per cent. of sugar in urine without differentiating them. In (*i*), a mixture of benzidine (m.p. 127° to 129° C), sodium perborate and K H phthalate (2:2:1), ground together, is put in a test-tube or on a slide and a little urine is added. In 2 min., development of a blue colour denotes a positive reaction. In (*ii*), a mixture of equal parts of benzidine and sodium perborate, ground together, is poured to a depth of 1 cm into a Kahn tube; 1 ml of urine is added, followed by 0·5 ml of glacial acetic acid. The liquid layers are mixed without disturbing the solid. In 2 min. a positive reaction is signified by a blue colour at the solid - liquid interface. Tap water, formaldehyde and $FeCl_3$ also give a blue colour. O. M. WHITTON

3137. **Determination of vitamin E in blood.** P. P. Nair and N. G. Magar (Dept. of Biochem., Inst. of Sci., Bombay). *J. Biol. Chem.*, 1956, **220** (1), 157–159.—A very sensitive, specific and simple method is described for the determination of vitamin E in plasma or serum. It depends on a colour reaction between the vitamin and molybdophosphoric acid. The extinction is determined spectrophotometrically at 725 mμ, and there is no interference from vitamin A, calciferol, cholesterol or carotenoids. The serum must be treated first with alkali to hydrolyse any tocopheryl esters because these do not react with the chromogenic reagent. J. N. ASHLEY

3138. **Fluorimetric determination of adrenaline and noradrenaline in plasma.** J. A. Richardson, A. K. Richardson and O. J. Brodie (South Carolina Med. Coll., Charleston, S.C., U.S.A.). *J. Lab. Clin. Med.*, 1956, **47** (5), 832–834.—In the method of Weil-Malherbe and Bone (*Brit. Abstr. C*, 1952, 306), modified reagents and procedure and the use of a Beckman DU spectrophotometer as a fluorimeter enable adrenaline and noradrenaline in plasma concn. down to 0·25 and 0·5 μg per litre, respectively, to be determined in a 15-ml blood sample. Recoveries of known amounts of the two compounds from dog plasma were 93·4 $\pm$11·5 and 90·3 $\pm$9·9 per cent., respectively.

W. H. C. SHAW

3139. **The colorimetric estimation of chlorpromazine in biological fluids.** H. Leach and W. R. C. Crimmin (Group Lab., Caernarvon, Wales). *J. Clin. Pathol.*, 1956, **9** (2), 164–165.—*Procedure for urine*—Extract 20 ml of urine and 1 ml of *N* NaOH with ether (4 $\times$ 20 ml), wash the pooled extracts with 10 ml of 0·2 *N* NaOH, followed by 10 ml of water. Shake the extract vigorously with 10 ml of 0·1 *N* H_2SO_4, allow to stand for 5 min., separate the acid extract and remove the ether by warming slightly and aerating for a few sec. Use 6 ml of H_2SO_4 soln. for extraction if less than 1 mg per litre of chlorpromazine (**I**) is present. If intractable urine - ether emulsions form, transfer to a centrifuge and treat as for blood. *Procedure for blood*—For free **I**, warm 5 ml of oxalated blood and 5 ml of 50 per cent. KOH in a 50-ml centrifuge tube on a boiling-water bath for 2 min., with frequent and vigorous shaking. Cool, add 10 ml of water, shake well with 20 ml of ether, centrifuge, transfer the ether layer to a separating funnel and repeat the ether extraction three times more. Wash the combined ether extracts with NaOH and water, as for urine, and extract with 6 ml of 0·1 *N* H_2SO_4. Take 4 ml of the acid extract for the colour test. For total **I**, heat 5 ml of blood and 5 ml of conc. HCl in a boiling-water bath for 5 min., cool, make alkaline and extract with ether; continue as for free **I**. *Estimation*—To 4 ml of acid extract add 2 ml of 50 per cent. H_2SO_4, mix well and add 0·2 ml of 2 per cent. $Fe(NO_3)_3.9H_2O$. Read the red colour at 530 mμ against a water blank. Prepare a calibration curve for the range 5 to 100 μg of **I** in 4 ml of 0·1 *N* H_2SO_4.

H. F. W. KIRKPATRICK

3140. **Rapid paper chromatography of carbohydrates and related compounds.** H. T. Gordon, W. Thornburg and L. N. Werum (Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 849–855.—A solvent mixture of *iso*propyl alcohol, pyridine, glacial acetic acid and water (8:8:1:4) tends to separate carbohydrates and their derivatives into groups of similar structure, all moving within a narrow R_F range. Inorganic salts do not normally interfere with the movement of the organic compounds on the chromatogram and R_F values are highly reproducible. Improved specific colour reagents are described for the semi-quant. estimation of carbohydrates, polyhydric alcohols, aldonic and uronic acids, nucleosides, phosphate esters and other derivatives. Data for $\simeq$ 70 compounds are listed. G. P. COOK

3141. **Observations on the periodide method for the estimation of choline.** G. R. Webster (Guy's Hosp. Med. Sch., London). *Biochim. Biophys. Acta*, 1956, **20** (2), 432–433.—In a re-examination of this method it is shown that the acetyl, propionyl, butyryl, acetyl-β-methyl and benzoyl esters of choline are pptd. as periodides in a similar manner to choline and the ppt. have molar extinction values at 365 mμ in chloroform equivalent to that for choline. Phosphoryl- and glycerophosphoryl- choline are not pptd., but interfere in

the pptn. of choline periodide, and it is recommended that amounts of these two compounds similar to those in test soln. should be added to the choline standards. With the procedure recommended, 0·05 to 0·5 μmole of choline can be estimated. Beer's law is not obeyed. *Procedure*—To 0·5 ml of sample containing 5 per cent. w/v of trichloroacetic acid in a pointed centrifuge tube add 0·2 ml of KI_3 reagent (15·7 g of iodine and 20 g of KI in water to 100 ml). Stir, cool in ice, centrifuge and remove the supernatant liquid in the manner described by Appleton *et al.* (*Anal. Abstr.*, 1954, **1**, 758). Dissolve the ppt. in 10 ml of chloroform and read the extinction at 365 mμ against an appropriate blank. W. H. C. SHAW

3142. **Acetylcholine in the brain. II. Chemical measurement of choline esters.** W. E. Stone (Wisconsin Univ. Med. Sch., Madison, U.S.A.). *Arch. Biochem. Biophys.*, 1955, **59** (1), 193–198.—Methods are detailed for the extraction of brain tissue, purification of the extract with lead acetate and removal of excess of Pb″. Choline is then added to the purified extract and co-pptd. with the acetylcholine by tungstophosphoric acid from the solution buffered with malonic acid. The ppt. is collected, re-pptd. by similar treatment, and the acetylcholine is determined colorimetrically by the hydroxylamine - $FeCl_3$ reaction. The slightly high results given by the proposed method as compared with those obtained by a frog-muscle assay are considered to be due to traces of interfering chromogenic material. W. H. C. SHAW

3143. **A simple method for assaying adenosine triphosphate and adenosine diphosphate in mixtures.** W. J. Bowen and T. D. Kerwin (Nat. Inst. of Health, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1956, **220** (1), 9–14.—A method is described for the determination of adenosine triphosphate and adenosine diphosphate, either singly or together. The determination of adenosine triphosphate depends on direct measurement of the third phosphate group after it is hydrolysed by once-precipitated myosin B (which acts as adenosinetriphosphatase) in the presence of EDTA. The EDTA accelerates the dephosphorylation of the triphosphate and also completely inhibits myokinase (adenylate kinase) which may be present in the myosin-B preparation. The myosin B completely and rapidly converts adenosine triphosphate into the diphosphate and the liberated PO_4''' is a mole for mole measure of the triphosphate originally present. Once the adenosine triphosphate content is known, or if the triphosphate is absent, the adenosine diphosphate content is ascertained by combining the action of myosin B and myokinase on another sample of the solution or mixture. In the absence of EDTA and in the presence of $CaCl_2$, myokinase rapidly dismutes adenosine diphosphate into adenosine triphosphate and adenosine monophosphate. With myosin present, the adenosine triphosphate so formed is continually dephosphorylated, and finally all of the triphosphate, or triphosphate plus diphosphate, is converted into adenosine monophosphate and PO_4'''. The adenosine diphosphate content is then equivalent to the PO_4''' split off in excess of twice that removed by myosin in the presence of EDTA. J. N. ASHLEY

3144. **Determination of pipecolic acid in biological materials.** O. O. Silberstein, R. M. Adjarian and J. F. Thompson (Agric. Res. Ser., Ithaca, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 855–857.—The method is based on the colour formed between pipecolic acid and ninhydrin under acid conditions. The reaction is subject to interference by salts and α-amino acids, but these are separated from the pipecolic acid by ion-exchange chromatography. In determinations of standard pipecolic acid (15 μg), duplicates agree within 1 per cent. The mean recovery of added pipecolic acid from rabbit urine and turnip-leaf extracts was 101 per cent. G. P. COOK

3145. **Conductimetric determination of amino acids and their derivatives.** M. Pascal (Inst. Chim., Univ. Montpellier, France). *Chim. Anal.*, 1956, **38** (6), 201–206.—Conductimetric titration of amino acids having primary, *sec.*- or *tert.*-amino groups is carried out by running the amino-acid solution into standard NaOH solution. A good intersection is obtained of the straight portions of the plot of conductivity *vs.* vol. added. For compounds such as glutamic acid or tyrosine, with two acid functions with dissociation constants differing by a factor of 10, two breaks are obtained. An attempt to titrate the amino groups with $HClO_4$, even in aq. ethanol or aq. acetic acid, leads to a continuous plot and though the differential curve has a min. at the equivalence point its exact position cannot be found. If an amino-acid solution is run into standard cupric acetate, the conductivity falls until all the copper has been complexed and a good intersection of straight portions is obtained. The Cu to amino-acid ratio is 1:2 for a mono-amino mono-acid and 1:1 for glutamic acid and hydroxyethylaminediacetic acid. 2-Morpholinone, hippuric acid, urea, and compounds without an amino group α- to carboxyl give no complex. In the presence of electrolytes it is better to use back-titration and, after addition of amino acid to an excess of NaOH, the NaOH is back-titrated with a standard solution of an amino acid of p*K* similar to that of the subject acid. A compound like 2-morpholinone can be hydrolysed by heating with an excess of standard NaOH which is then titrated. E. J. H. BIRCH

3146. **Quantitative micro-estimation of α-amino acids.** E. Pfeil and H.-J. Goldbach (Univ. Marburg, Germany). *Klin. Wochschr.*, 1956, **34** (7–8), 194–195.—The method is based on the copper complex method of Woiwod (*Biochem. J.*, 1949, **45**, 412). The amino-acid soln. is spotted on a strip of filter-paper and the spot is moistened with 0·025 ml of $CuSO_4.5H_2O$ soln. (39·3 mg in 100 ml of H_2O). After drying, the paper is stood in a trough containing 20 per cent. w/v $Na_2HPO_4.12H_2O$ and an ascending chromatogram is run for 30 to 40 min. To prevent traces of copper phosphate being carried with the solvent, a "barrier" consisting of a band, 1 cm wide, of 20 per cent. Na_2HPO_4 soln. is placed immediately in front of the sample spot. After drying, the chromatogram is sprayed with a 0·5 per cent. aq. soln. of Na diethyldithiocarbamate (**I**) when the copper complexes show a dark-brown to black colour. The strip containing the copper is cut out, placed in a small separating funnel and 10 ml of aq. NH_3 (1 part of conc. aq. NH_3 + 1 part of H_2O), 10 ml of amyl alcohol - chloroform (1:1) and 2 ml of **I** are added and the mixture is well shaken. After separation, the lower layer is run through a dry filter-paper and the colour is measured at 435 mμ against a blank. H. F. W. KIRKPATRICK

3147. **Modified ultra-violet spectrophotometric micro-method for determination of amino acids and peptides as copper complexes.** A. Cherkin, H. Wolkowitz and M. S. Dunn (Univ. Calif., Los Angeles, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 895–896.—The method of Spies (*J. Biol. Chem.*, 1952, **195**, 65) was studied, and the procedure was subjected to a few minor modifications in order to reduce the blank value and increase the accuracy with samples of < 1 μmole. G. P. Cook

3148. **Receptor substances for phage T 5. IV. A simple method for the quantitative estimation of amino acids and its application for comparison between the receptor substance and various mutation products.** G. Koch and W. Weidel (Max Planck Inst. for Biology, Tübingen, Germany). *Hoppe-Seyl. Z.*, 1956, **303**, (3–6), 213–223.—A simple two-dimensional paper-chromatographic method is described for the separation and estimation of the 2:4-dinitrophenyl deriv. of the amino acids; a butanol - aq. NH_3 or propanol - aq. NH_3 system is used for one direction and a 1·5 *M* phosphate buffer of pH 6 for the other. The 2:4-dinitrophenyl deriv. are prepared by treating the hydrolytic products with fluorodinitrobenzene in a Na_2CO_3 - $NaHCO_3$ buffer soln. at a pH of 9. For quant. results, the individual acids are extracted from the paper with water (3 × 5 to 10 ml) at 25° C, and the extinction is measured at 360 mμ (for proline 385 mμ). When the method was applied to hydrolysates obtained from lipoglycoproteins derived from the T 5 receptor substances from *Escherichia coli* B and its inactive receptor analogue from *E. coli* B/1·5, no difference in amino-acid composition was found. G. R. Whalley

3149. **Chamber size and R_F values of amino acids.** R. A. Clayton (George Washington Univ. Sch. Med., Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 904–906.—A term "critical volume" is introduced to define the volume of solvent necessary to saturate a specific chamber under a given set of experimental conditions. It was found that when the amount of developing solvent used exceeded the critical volume, the R_F values were constant and at a minimum; below the critical volume the R_F values were at a constant maximum. The *n*-butanol - acetic acid - water system was used for the study. G. P. Cook

3150. **Differentiation of some natural amino acids by their capacity to reduce vanadic acid to a vanadyl salt.** J. Garcia-Blanco and A. M. Pascual-Leone (Lab. Fisiol. Gen., Fac. Med. Valencia, Spain). *Rev. Española Fisiol.*, 1955, **11**, 149–152.—The reagent consisted of ammonium vanadate (10 mg) mixed with water (1 ml), with conc. H_2SO_4 (9 ml) then added slowly. To 1 ml of amino-acid soln. was added 1 ml of reagent. A positive reaction is characterised by a change of colour from orange to blue. The amino acids that gave positive reactions and the amounts necessary to reduce 1 mg of vanadate were—cysteine 0·25 to 0·125, cystine 0·5 to 0·25, methionine 0·5 to 0·25, and tyrosine 4 mg. Tryptophan (0·125 mg) gave an intense dark-brown colour. No reaction was given by glycine, alanine, serine, valine, leucine, *iso*-leucine, phenylalanine, lysine, arginine, aspartic acid, glutamic acid or histidine.

Nutrition Abstr. and Rev.

3151. **Interaction of substances during the process of paper chromatography.** M. T. Beck and P. Ébrey (Szeged Univ., Hungary). *Biochim. Biophys. Acta*, 1956, **20** (2), 393.—The occurrence of diffuse spots or the appearance of separate spots (artefacts) in the paper chromatography of amino acids is discussed. It is considered that these may be due to molecular interaction between solvent and amino acid or between two amino acids, and so for accurate chromatography the use of amino acid - metal complexes instead of free amino acids is preferable.

W. H. C. Shaw

3152. **Colorimetric determination of hydroxyproline.** D. S. Miyada and A. L. Tappel (Univ. Calif., Davis, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 909–910.—Some of the principal factors that influence the colorimetric determination of hydroxyproline by the method of Neuman and Logan (*J. Biol. Chem.*, 1950, **184**, 299) were studied. An improved procedure and its application to the determination of hydroxyproline in gelatin and collagen are presented. G. P. Cook

3153. **Indirect polarographic determination of methionine.** Takeji Noto and Manabu Matsuoka (Tanabe Pharm. Co., Kashima-cho, Higashiyodogawa-ku, Osaka). *Japan Analyst*, 1956, **5** (3), 141–144.—Methionine (**I**) and its oxidation products (methionine sulphoxide and methionine sulphone) are polarographically inactive in dil. HNO_3 soln. Lead dioxide quant. oxidises **I** to give Pb^{++}, equiv. in amount to the **I**, which are polarographically determined by the usual method. A linear working curve is provided for 5×10^{-4} to 5×10^{-5} mole of **I**. Lead dioxide (20 mg) is washed with 7 *N* HNO_3 (2 ml), water and ethanol, then added to **I** soln. ($\simeq 10^{-5}$ mole in 2 ml of $\simeq$ 3·5 *N* HNO_3) and the mixture is shaken for 20 to 40 min. at room temp. The product is made up to 20 ml with water after addition of 7 *N* HNO_3 (2 ml) and 0·5 per cent. gelatin soln. (0·4 ml). The soln. is submitted to polarography. A blank value should be subtracted. The relative error is < 4 per cent. This method is especially suitable for the determination of **I** in a mixture with its oxidation products. K. Saito

3154. **Fluorimetric micro-method for determination of tryptophan.** G. D. Miller and J. A. Johnson (Kansas State College, Manhatten, Kan., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 884–887.—Tryptophan is separated from other amino acids by an ion-exchange procedure, and the fluorescent intensity of the substances formed by its reaction with glucose under optimum conditions is measured. Recoveries of tryptophan from the chromatographic column were 100 ± 2 per cent. and the standard error of the whole procedure was ± 3 per cent. for 12 μg of tryptophan. G. P. Cook

3155. **Iodimetric determination of tyrosine, tryptophan and methionine in soluble unhydrolysed proteins.** J. Baraud and L. Genevois (Lab. de Chim. Biol., Fac. des Sci., Bordeaux). *Bull. Soc. Chim. France*, 1955, (11–12), 1499–1501.—The iodimetric method for tyrosine, tryptophan and methionine (*cf. Anal. Abstr.*, 1956, **3**, 2538) is applied to unhydrolysed proteins whose purification from various sources is described. *Procedure*—Iodine soln. (0·01 *N*) (50 ml), citric buffer (pH 6) (10 ml) and the protein soln. (25 ml) are placed in two stoppered Erlenmeyer flasks. The first is allowed to stand for 2 hr. and is then titrated with 0·01 *N* $Na_2S_2O_3$, giving a titre of iodine consumed for tyrosine (4 equiv. per mol.) plus tryptophan

(6 equiv. per mol.) plus methionine (2 equiv. per mol.) plus a histidine correction. After removal of excess of iodine the solution is made strongly acid; iodine is thus liberated from the methionine complex and is then titrated. The correction for histidine, which is proportional to time, is obtained by titrating the contents of the second flask after 3 hr. and subtracting twice the difference in titre from the 2-hr. titration. The determination is also repeated with the buffer at pH 4, and after 2 hr. the strongly acidified mixture is titrated with 0·01 *N* $Na_2S_2O_3$, to give the titre for tryptophan. That the results accord with investigations on hydrolysed proteins is taken as evidence that the ω-groups of the amino-acid residues in proteins are quant. functional. E. J. H. Birch

3156. **Micro-determination of *p*-aminohippuric acid in serum from venous and capillary blood.** M. Fritsch (Univ. Frauensklinik, Wilhelms Univ., Münster, Westphalia, Germany). *Klin. Wochschr.*, 1956, **34** (19–20), 541–544.—To 0·2 ml of serum add 1·5 ml of $CdSO_4$ soln. and 5 ml of water. Add 0·5 ml of *N* NaOH, allow to stand for 10 min. and centrifuge. To 5 ml of supernatant add 0·5 ml of 2 *N* HCl and 0·5 ml of freshly prepared 0·2 per cent. $NaNO_2$ soln. and shake well. After 5 min. add 0·5 ml of 2 per cent. sulphamic acid with shaking, then allow to stand for 5 min. and add 0·5 ml of 1 per cent. soln. of N-ethyl-1-naphthylamine hydrobromide in absolute ethanol. After allowing the soln. to stand for 30 min. at 15° to 20° C, read the red colour at 535 mμ and obtain the concn. of *p*-aminohippuric acid from a standard curve. H. F. W. Kirkpatrick

3157. **A new method for the examination of mixtures of diastereoisomeric peptides.** S. Blackburn and P. Tetley (Wool Ind. Res. Assn., Headingley, Leeds, England). *Biochim. Biophys. Acta*, 1956, **20** (2), 423–424.—The method of Moore and Stein (*Brit. Abstr. C*, 1952, 62), in which chromatography on prepared Dowex-50 resin is used, is adapted for the separation of diastereoisomeric peptides which may result from the isomerisation of dipeptides synthesised from optically active amino acids. In the example given, the separation of L-leucyl-L-tyrosine and D-leucyl-L-tyrosine is detailed and the determination of each compound in fractions of the eluate by application of the ninhydrin colour reaction and measurement of the extinction at 570 mμ is described. W. H. C. Shaw

3158. **Two-dimensional electrophoresis of serum proteins.** O. Smithies and M. D. Poulik (Dept. Hyg. and Preventive Med., Univ. Toronto, Canada). *Nature*, 1956, **177**, 1033.—The serum proteins, *e.g.*, in 0·01 ml of normal human serum, are separated first according to their free-soln. mobilities on a strip of S. & S. 589 YD filter-paper 5 mm wide; a buffer (pH 8·55) of ionic strength approx. 0·1, prepared from Michaelis stock soln. (*cf. Biochem. Z.*, 1931, **234**, 139) by adding HCl, is used. The strip is then inserted into a starch gel 12 cm in width, and a second electrophoresis is carried out at right angles to the first, so that the proteins are further separated according to their molecular sizes. O. M. Whitton

3159. **Further studies on the absorption spectra of steroids in "100 per cent." phosphoric acid.** W. J. Nowaczynski and P. R. Steyermark (Hôtel-Dieu Hosp., Montreal, Canada). *Canad. J. Biochem. Physiol.*, 1956, **34** (3), 592–599.—The use of absorption spectra in "100 per cent." phosphoric acid (*Anal. Abstr.*, 1956, **3**, 1119) in investigations of steroids has been further studied with 67 additional compounds. The absorption maxima and minima of these compounds are tabulated and the characteristic absorption of various functional groups is discussed. Corticosteroids and their metabolites that could be identified by this method included hydrocortisone and cortisone and their tetrahydro derivatives, and aldosterone.

H. F. W. Kirkpatrick

3160. **New solvent systems for the resolution of corticosteroids by paper chromatography.** W. R. Eberlin and A. M. Bongiovanni (Philadelphia Childrens Hosp., Pennsylvania Univ., Pa., U.S.A.). *Arch. Biochem. Biophys.*, 1955, **59** (1), 90–96.—The simplified procedure described allows the Bush method of separation of $C_{(21)}$ steroids on paper chromatograms (*Brit. Abstr. C*, 1952, 107) to be used at room temp. R_F values are listed for 18 corticosteroids and 10 corticosteroid acetates in four modified Bush solvent systems and in four new systems in which the stationary phase is *tert.*-butyl alcohol or a mixture of methanol and *tert.*-butyl alcohol. The recommended solvent systems, used in combination, permit increased resolution of steroid mixtures and structural characterisation of unknown steroids from the differences in chromatographic behaviour.

W. H. C. Shaw

3161. **A new colour reaction for 17-hydroxy-corticosteroids and related compounds.** P. R. Steyermark and W. J. Nowaczynski (Hôtel-Dieu Hosp., Montreal, Canada). *Arch. Biochem. Biophys.*, 1955, **59** (1), 1–4.—The P_2O_5 - H_2SO_4 reagent proposed gives violet colours (λ max., 500 to 560 mμ) with Δ^4-17:21-dihydroxy-3:20-diketonic steroids of the $C_{(21)}$ series under standard conditions. Certain compounds having a C-20 hydroxyl group also give a positive reaction. Calibration with three typical corticosteroids is rectilinear with up to 40 μg per ml and is satisfactory for concn. down to 7 μg per ml. *Reagent*—Add 50 g of P_2O_5 to 100 g of conc. H_2SO_4. Stir and filter through glass wool. *Procedure*—Add 3 ml of reagent to the dry steroids and heat for 40 min. at 55° to 60° C. Determine the absorption spectrum from 400 to 600 mμ against a blank treated similarly.

W. H. C. Shaw

3162. **Colour test for 17-hydroxy-20-keto-21-methylsteroids.** W. J. McAleer and M. Kozlowski (Merck & Co. Inc., Rahway, N.J., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **62** (1), 196–197.—The test described is specific for 17α-hydroxy-20-keto-21-methylsteroids and was developed for use on paper chromatograms on which 10 to 20 μg per sq. cm can be detected. *Procedure*—Spray the thoroughly dry chromatogram with a solution of 25 g of vanillin in 100 ml of 85 per cent. H_3PO_4. Heat in an oven at 70° C for 20 minutes. Reactive steroids give an orange spot on a yellow background.

W. H. C. Shaw

3163. **A method for the determination of oestriol, oestrone and oestradiol-17β in human urine by partition chromatography and colorimetric estimation.** W. S. Bauld (Dept. of Metabolism, Montreal Gen. Hosp., Canada). *Biochem. J.*, 1956, **63** (3), 488–495.—A method is described for the extraction, separation, purification and determination of oestriol, oestrone and oestradiol-17β in human urine. The method involves acid hydrolysis, ether

extraction, separation of oestriol from oestrone and oestradiol-17β by distribution between benzene and water, purification of oestriol by saponification and column partition chromatography, and separation and purification of oestrone and oestradiol-17β by column partition chromatography and saponification. The purified fractions are determined colorimetrically by an improved Kober reaction, with a spectrophotometric correction for non-oestrogen chromogenic material. The specificity, accuracy, precision and sensitivity of the method are discussed. J. N. ASHLEY

3164. **Some observations on the sulphuric acid colour reaction for the estimation of pregnanediol.** A. I. Klopper (Med. Res. Council, Edinburgh Univ., Scotland). *J. Endocrin.*, 1956, **13** (3), 291–295. Factors affecting the intensity of colour given by pregnanediol and pregnanediol diacetate with conc. H_2SO_4 are investigated. From a study of the rate of colour development and the effect of heat and addition of oxidising or reducing agents, it is concluded that the conditions for colour development must be rigidly standardised and, to eliminate variations with different samples of H_2SO_4, the addition of 0·03 g of sodium sulphite to 10 ml of acid is recommended. The lack of specificity of the method is considered a disadvantage.
W. H. C. SHAW

3165. **The estimation of peptidase activity in the white blood cells by paper chromatography.** F. Nour-Eldin and J. F. Wilkinson (Royal Infirmary, Manchester, England). *J. Clin. Pathol.*, 1956, **9** (2), 175–176.—A method is described by which peptidases are extracted from white blood cells and the activity of the extracts estimated by incubation with substrates containing glycylglycine, glycylglycylglycine, and leucylglycylglycine, the glycine liberated being determined by paper chromatography. H. F. W. KIRKPATRICK

3166. **Turbidimetric measurement of acid mucopolysaccharides and hyaluronidase activity.** N. Di Ferrante (Rockfeller Inst. for Med. Res., New York, U.S.A.). *J. Biol. Chem.*, 1956, **220** (1), 303–306.—A simple, rapid and reproducible method is described for the determination of (*a*) 10 to 200 μg of isolated acid mucopolysaccharides, and (*b*) hyaluronidase activity. It depends on the formation of relatively insol. complexes between isolated acid mucopolysaccharides and cetyltrimethylammonium bromide. The turbidity produced is proportional to the amount of acid mucopolysaccharide, and the extinction of the turbid solution is determined spectrophotometrically, with a photomultiplier attachment, at 400 mμ. Hyaluronidase activity is determined by measuring the turbidity produced by an acid mucopolysaccharide before and after treatment, under specified conditions, with the enzyme. The advantages of using cetyltrimethylammonium bromide as the reagent are discussed. J. N. ASHLEY

See also Abstracts 2982, 2995, 3088, 3089, 3096, 3220, 3239.

Drugs

3167. **Ion-exchange separation of morphine prior to its determination in *Papaver somniferum*.** C. H. Van Etten, F. R. Earle, T. A. McGuire and F. R. Senti (U.S. Dept. Agric., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 867–870.—The morphine is separated from impurities by an ion-exchange system in which both anion- and cation-exchange resins are used. The impurities removed are various anions, neutral substances, bases, cations and ampholytes. The morphine is finally measured colorimetrically, by u.v. absorption or by titration. An average recovery of 98 per cent. and a standard deviation of $\pm$ 1·9 was obtained on 18 samples containing 5 to 20 mg of pure morphine. The analysis of opium and various extracts from the poppy plant gave results that were lower than those obtained by a colorimetric and a solvent-extraction method, but 10 to 40 per cent. higher than those methods involving crystallisation.
G. P. COOK

3168. **Titration of drugs and chemicals in non-aqueous solution. VIII. Determination of tropan alkaloids in glacial acetic acid.** Tetsu Kashima, Haruyo Asahina and Yoshihiko Shiuchi (National Hyg. Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (5), 586–588.—Tropan alkaloids, including cocaine (**I**), tropacocaine (**II**), homatropine (**III**), atropine (**IV**) and hyoscine (**V**) can be titrated with $HClO_4$ in glacial acetic acid, with crystal violet as indicator. Their hydrochlorides or hydrobromides can also be titrated, with an error $<$ 0·05 per cent., in the presence of mercuric acetate. The basicity of these alkaloids decreases in the sequence **I**, **V**, **II**, **III** and **IV**. K. SAITO

3169. **A new approach to the assay of alkaloidal crude drugs. II. Ipecac.** E. Brochmann-Hanssen Calif., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (5), 344–347.—An ion-exchange method described for the assay of ipecacuanha for phenolic and non-phenolic alkaloids gives results that are higher than those obtained by the assay of the U.S.P. XV and are of slightly greater precision. *Procedure*—Shake the finely powdered sample (200 mg) with Dowex 50-X_2 (H^+ form) (1 g) and H_2O (25 ml) for 15 min. Transfer to a suitable tube and remove the crude drug residue by a backwash with H_2O. Elute with 4 *N* aq. NH_3 in 70 per cent. methanol and pass the eluate through a column (10 cm or 15 cm in length) of Dowex 1-X_1 (OH^- form). Collect 100 ml and determine the non-phenolic alkaloids by spectrophotometry at 285 mμ; methanolic NH_3 soln. that has passed through the same anion-exchange column is used as a blank. Wash the anion-exchange column with H_2O and elute with 0·1 *N* acetic acid. Collect 100 ml and determine the phenolic alkaloids in a 10-ml aliquot by coupling with diazotised *p*-aminoacetophenone in alkaline soln. and measuring the extinction at 495 mμ. A. R. ROGERS

3170. **Colorimetric determination of ephedrine.** Naokazu Sakota, Taneyoshi Yu, Yoshimi Okada and Hiroko Urabe (Dainippon Zoki Inst., Higashisumiyoshi-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (2), 279–281.—The colorimetric determination of ephedrine (**I**) was studied by the use of Folin's reagent (**II**) (*J. Biol. Chem.*, 1951, **193**, 265) in the presence of Cu. The sample soln. (0·5 ml) containing 0·2 to 2·0 mg of **I** is mixed with freshly prepared basic Cu soln. (0·1 *N* NaOH containing 0·01 per cent. of $CuSO_4$, 0·02 per cent. of Na K tartrate and 2 per cent. of Na_2CO_3) (2·5 ml), and **II** (0·25 ml) is added after 20 min. The extinction coeff. (660 mμ) of the resulting soln. is measured after 30 min. The optimum pH value is $\simeq$ 10. Compounds having

an aromatic hydroxy group appear to interfere with the coloration. Similar compounds, such as methamphetamine and chloromethamphetamine, fail to show the colour reaction. K. SAITO

3171. **Compleximetric methods in organic analysis. I. Precipitations with bismuth potassium iodide.** B. Buděšínský (Pharm. Research Inst., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (1), 146–154.—The ppt. obtained by the action of bismuth potassium iodide on a number of organic bases are described. Weak bases, *e.g.*, caffeine, 8-methylcaffeine and theophylline, give, in strongly acid solution, ppt. of the formula $X^{n+}[(BiI_4)^-]_n$, strong (quaternary) bases and, *e.g.*, hexamine, give ppt. of the formula $(X^{n+})_3[(BiI_4)^-]_{2n}I^-_n$, whilst moderately strong bases ($pK \simeq 9$), *e.g.*, codeine, amidopyrine and phenazone, give ppt. with a formula intermediate between these. The composition of the ppt. is controlled by careful adjustment of the pH. For the quant. determination of the bases, a known excess of bismuth potassium iodide is added at the appropriate pH, the ppt. is filtered off and the excess of Bi is titrated with EDTA; the disappearance of the yellow bismuth iodide colour denotes the end-point. Bases that form insoluble iodides are estimated in 20 per cent. acetic acid soln. in which the iodides are not insoluble. Caffeine and 8-methylcaffeine can be determined in the presence of, *e.g.*, amidopyrine, phenazone and quinine by first pptg. the 8-methylcaffeine with potassium mercuri-iodide. P. S. STROSS

3172. **Identification of 8-hydroxyquinoline in smoke from tobacco treated with 8-hydroxyquinoline potassium hydrogen sulphate.** E. Wegner (Bundesanst. Tabakforschung, Forchheim, Karlsruhe, Germany). *Arzneimittel-Forsch.*, 1956, **6** (5), 299–300.—The detection and identification of 8-hydroxyquinoline (**I**) in the smoke from tobacco preserved with **I** - $KHSO_4$ (Chinosol) are described. *Procedure*—Pass the smoke from 25 g of tobacco through cotton wool and suspend the tarry phase in water (500 ml). Neutralise with Na_2HPO_4 and steam-distil. Free the distillate from interfering substances by successive ether extractions, first after acidifying (conc. HCl) and then after rendering alkaline (conc. NaOH). Any **I** remains in the aq. phase. Acidify, neutralise with excess of $NaHCO_3$, and extract with ether. Dry the extract, remove the ether, and dissolve the residue in ethanol. Test the ethanolic soln. for **I** by ascending paper-chromatography, with 15 per cent. acetic acid as solvent and 1 per cent. ethanolic $FeCl_3$ as developer (blue spot). J. P. STERN

3173. **Chromatography of the 2:4-dinitrophenylhydrazones of some aldehydes and ketones in tobacco smoke.** D. A. Buyske, L. H. Owen, P. Wilder, jun., and M. E. Hobbs (Duke Univ., Durham, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 910–913.—Tobacco smoke was collected at liquid-air temp., and the unfractionated raw smoke was converted into 2:4-dinitrophenylhydrazones. These were chromatographed on paper treated with dimethylformamide and developed with *n*-hexane. The phenylhydrazones of furfuraldehyde, formaldehyde, acetaldehyde, propionaldehyde, acetone, ethyl methyl ketone, diethyl ketone and butyraldehyde were separated and identified by comparative paper chromatography and their absorption spectra. About 10 per cent. by wt. of free aldehydes and ketones was present in the smoke. G. P. COOK

3174. **Podophyllum resin, Ph. I.** W. Mitchell (Stafford Allen & Sons Ltd., London). *Pharm. J.*, 1956, **176**, 133.—Specimens of podophyllum resin from *P. peltatum* gave results ranging from 44 to 48 per cent. of residue when the assay of the Ph. I was applied. The Ph. I requirement of 40 to 50 per cent. of podophyllotoxin (**I**) was not complied with, since the residues on crystallising from ethanol - benzene gave only 7 per cent. of **I** calculated on the original resin. Indian podophyllum from *P. hexandrum* gave results from 61 to 71 per cent. of residue yielding 42 to 46 per cent. of **I** calculated on the original resin. It is suggested that the material weighed should be described as "residue" or "extractive" instead of as **I** and that Indian podophyllum should be included in the Ph. I. N. E.

3175. **Separation of acetylated neomycins B and C by paper chromatography.** S. C. Pan and J. D. Dutcher (Squibb Inst. for Med. Res., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 836–838.—The acetylated neomycins B and C are separated by paper chromatography with a solvent system of butanol - pyridine - water (6:4:3); the R_F values for N-acetylneomycin B and C are 0·29 and 0·19, respectively. The spots are detected by conversion into the N-chloro derivatives followed by colour development with starch - KI spray reagent. A semi-quant. estimation, giving an error of $\simeq \pm 30$ per cent., can be made by cutting out and weighing the spots. G. P. COOK

3176. **Determination of griseofulvin in fermentation samples. I. Spectrophotometric assay.** G. C. Ashton and A. P. Brown (Glaxo Lab. Ltd., Stoke Poges, Bucks., England). *Analyst*, 1956, **81**, 220–224.—A method is described for the extraction of griseofulvin from fermentation broths of suitable *Penicillium* spp. and its subsequent spectrophotometric determination. Butyl acetate proved to be a suitable extracting solvent owing to its relative immiscibility with the whole broth, its failure to form emulsions and its high extracting property. The whole-broth sample (5 ml) is extracted twice only with 20-ml portions of butyl acetate, the combined extracts are diluted to 100 ml with the solvent and filtered. Aliquots of the filtrate are adjusted with the solvent to contain 5 to 15 μg of griseofulvin per ml and the extinction is measured at intervals of 2 mμ from 288 mμ to 300 mμ against the solvent. Calculation of the results from these measurements is based on quadratic curvature coefficients.

Appendix: Seven-point correction procedure. G. C. Ashton and J. P. R. Tootill. *Ibid.*, 1956, **81**, 225–227.—Preliminary expt. made to establish the reference graph obtained with pure griseofulvin in butyl acetate at 2-mμ intervals indicated no significant absorption of higher complexity than quadratic. Although quadratic irrelevant absorption can be detected and allowed for with four points, it was desirable that a larger number should be used, and seven readings were ultimately chosen. By establishing values for a standard soln. from 278 to 302 mμ at 2-mμ intervals and comparing successive groups of readings at seven wavelengths, the seven wavelengths most suitable were found to be 288 to 300 mμ in 2-mμ intervals. The calculation of the quadratic correction coefficients is described by reference to an example.

II. Isotope-dilution assay. G. C. Ashton. *Ibid.*, 1956, **81**, 228–231.—To confirm the results of the

spectrophotometric assay (Part I) and also to provide an alternative procedure for the determination of griseofulvin, an isotope-dilution assay with ^{36}Cl, which easily enters the griseofulvin molecule, has been developed. The labelled griseofulvin is prepared by submerged fermentation of the appropriate strain in a medium containing $K^{36}Cl$. In the isotope assay the whole-broth is quant. extracted with ether, the labelled griseofulvin (50 mg) is dissolved in 5 ml of dimethylformamide and is evaporated with the ethereal extract. The residue is treated with water, the pptd. griseofulvin is set aside overnight, collected by filtration, dissolved in benzene and purified chromatographically on an alumina column with benzene - ethanol (99 : 1) as eluent. After removal of the eluent by evaporation, the residue is dissolved in dimethylformamide and filtered, and the pptn. with water is repeated. The collected ppt. is dried at 150° C, and its radioactivity is compared with that of the label. A. O. JONES

3177. **Paper chromatography of the polymyxins.** A. G. Mistretta (American Cyanamid Co., Princeton, N.J., U.S.A.). *Antibiot. & Chemother.*, 1956, **6** (3), 196–198.—By using ascending paper-chromatography on Whatman No. 1 filter-paper developed with butanol - water - *iso*propylamine (125 : 60 : 4) for 6 to 18 hr., separation of polymyxin B (R_F 0·43) from polymyxin D (R_F 0·23) is achieved. After drying, the polymyxins are located on the papers by a bio-autographic technique on an agar medium seeded with *Brucella bronchoseptica*, ATCC 4617. The amino acids formed on hydrolysis of the antibiotics with 6 *N* HCl are best distinguished by development with 80 per cent. aq. methanol, 80 per cent. aq. *iso*propyl alcohol or butanol - acetic acid - water (20 : 3 : 20). W. H. C. SHAW

3178. **Colorimetric determination of kainic acid, the active principle of *Digenea simplex*.** Michiharu Miyasaki, Raitaro Haraoka, Kazuo Fujisaki and Akira Morimoto (Fujisawa Pharm. Ind. Ltd., Kashima-cho, Higashiyodogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (5), 477–479.—The determination of kainic acid ($C_{10}H_{15}O_4N.H_2O$) (**I**) (structure unknown) was studied by the use of its colour reaction with ninhydrin (**II**). The yellowish colour (max. absorption, 429 mμ) is unstable in aq. soln., but can be quant. extracted with benzene. α-Amino acids also react with **II** and are extracted (max. absorption 500 mμ) with benzene; these, however, can be transferred to an aq. layer by shaking the benzene soln. with a dil. basic soln. No significant interference results from the presence of sugar and inorganic salts in the amount usually found in *Digenea*. A sample soln. containing 20 to 100 μg of **I** is treated in the dark with Clark - Lub's buffer (pH 5·0) (0·5 ml), benzene (7 ml) and **II** (2 per cent., 2 ml) in a water bath (60° C) for 10 min. The product (before the separation of the two layers) is treated with *N* NaOH (1 ml) and the benzene layer is separated and diluted before being photometrically measured. K. SAITO

3179. **Paper electrophoresis and paper chromatography of various analgesics.** G. Wagner (Pharm. Chem. Inst., Greifswald Univ., Germany). *Arch. Pharm., Berlin*, 1956, **289** (1), 8–15.—Paper-chromatographic separation of salicylic acid, salicylamide and salicyl*iso*propylamide on alkaline paper is described. Electrophoretic separation of these compounds can be achieved in alkaline soln. The separation of salicylic acid and acetylsalicylic acid by electrophoresis occurs between pH 4·0 and 5·0. Phenazone, aminophenazone, methylaminophenazone and amidopyrine are separated on acid-washed paper in aqueous *n*-butanol. Phenazone and amidopyrine are separated by electrophoresis in 6 hr. Irgapyrin can be separated into its components in alkaline solution; phenylbutazone appears at the anode, whilst amidopyrine is attracted to the cathode. Full details of results under a range of conditions are given. C. A. FINCH

3180. **Photometric determination of antipyrin [phenazone] with *p*-dimethylaminobenzaldehyde.** M. Hahn, J. Kolšek and M. Perpar (Inst. organ. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1956, **151** (2), 104–108.—Phenazone (**I**) gives a salmon-pink colour with a soln. of *p*-dimethylaminobenzaldehyde (**II**) in aq. H_2SO_4. Beer's law is not obeyed, but a calibration curve can be applied for concn. < 0·15 per cent. of **I**; the limit of detection is ≃ 0·003 per cent. of **I**. The intensity of colour increases with time, with the temp. at which the colour develops and with the temp. at which measurement is made. Acetanilide, acetylsalicylic acid, phenacetin and amidopyrine do not interfere. *Reagent*—Dissolve **II** (0·5 g) in a mixture of H_2SO_4 (8·5 g) and H_2O (8·5 ml). *Procedure*—Mix an aq. soln. of the sample (5 ml, containing ≃ 7·5 mg of **I**) with the reagent (5 ml). After 60 min., measure the extinction at 513 mμ. A. R. ROGERS

3181. **Improvement on the volumetric determination of isoniazid and its tablets.** Zen'ichiro Kochi (Osaka Factory, Takeda Pharm. Ind. Ltd., Jusonishino-cho, Higashiyidogawa-ku, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (6), 748–750.—Experimental conditions for the oxidation of isoniazid with $KBrO_3$ in KBr were examined and it was found that the reaction depends on the concn. of HCl (optimum, 0·70 to 0·86 *N*). Care should be taken to keep the reaction time and temp. constant. With a carefully controlled procedure, the deviation was decreased to within 0·2 per cent. for a sample of purity > 99·5 per cent. K. SAITO

3182. **A colorimetric method for the detection and determination of certain acid halide and acid anhydride compounds [anticholinesterases].** D. J. Marsh and E. Neale (Chem. Defence Exp. Estab., Porton Down, Wilts., England). *Chem. & Ind.*, 1956, (22), 494–495.—Acid halide and acid anhydride compounds, such as organic phosphoro- and phosphono-fluoridates, pyrophosphates, etc., can be detected and determined by reaction with H_2O_2 and aromatic bases of the benzidine type in alkaline soln. A coloured material is produced. The procedures for determination of *iso*propyl methylphosphonofluoridate (Sarin) (**I**), di*iso*propyl phosphorofluoridate (DFP) (**II**) and tetraethyl pyrophosphate (TEPP) (**III**) are given. The reagent is prepared by mixing (*i*) aq. acetone buffer [made by dissolving KH_2PO_4 (16 g) and KOH (9 g) in H_2O, diluting to 1 litre and mixing with an equal volume of acetone], (*ii*) 1 per cent. w/v soln. of H_2O_2, and (*iii*) *o*-dianisidine hydrochloride (1·3 per cent. aq. soln.) in the proportions 23 : 1 : 1 by vol. for **I**, and 23 : 3 : 1 by vol. for **II** and for **III**. To each of a number of 25-ml calibrated flasks are added 20 ml of the reagent and then 0 to 2 ml of **I**, **II** or **III**. The soln. is made up to the mark with reagent and mixed thoroughly. After 10 min. for **I**, 30 min. for **II**, and 20 min. for **III**, the colour is read on the Spekker absorptiometer,

with 1-cm cells and No. 601 (spectrum violet) filters. The reference cell is filled with reagent. A calibration curve is prepared from standard solutions of **I**, **II** or **III** in *iso*propyl alcohol (preferably not more than 2 ml; aliquots are taken so that a range of 0 to 300 μg is obtained). The precision of the method is $\pm$ 1 per cent. O. M. WHITTON

3183. **Determination of hexachlorophene in liquid soaps.** R. F. Childs and L. M. Parks (Sch. Pharm., Univ. of Arizona, Tucson, Ariz., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (5), 313–316.—In this spectrophotometric method, irrelevant absorption due to the soap base is eliminated by measuring the difference in extinctions at pH 3 and 8. *Procedure*—Dilute the sample (5 g) to 100 ml and dilute a 25-ml aliquot to 100 ml with 90 per cent. methanol. Dilute one 15-ml aliquot to 50 ml with 0·3 *M* acetic acid in 90 per cent. methanol and another 15 ml to 50 ml with 90 per cent. methanol. Measure the difference in the extinctions of the two soln. at 312 mμ, and calculate the concn. of hexachlorophene by the use of a calibration curve. A. R. ROGERS

3184. **Interference from excipients in the ultra-violet spectrophotometric assay of tablets.** H. Aasness (Gov. Pharm. Lab., Oslo, Norway). *Medd. Norsk Farm. Selskap*, 1955, **17** (4–5), 254–273.—In a study of the interference to be expected from some excipients in the u.v. spectrophotometric assay of tablets, absorption curves are given of soln., or filtered extracts, of lactose, potato starch, Mg stearate, powdered talc and gelatin in water, 96 per cent. w/v ethanol and ether. Similar curves are also given for extracts of "blank" granules, prepared from the same excipients, in the following solvents—water, 0·1 *N* HCl, 0·1 *N* NaOH, absolute (and 96 and 70 per cent. w/v) ethanol, methanol, *iso*propyl alcohol, butanol, ether, $CHCl_3$ and light petroleum. A procedure is suggested for evaluating the max. interference to be expected, based on the extinction at 250 mμ and on the solvent employed, the concn. of excipients by the extraction of the tablet, the ratio of the wt. of excipient to that of the therapeutic substance, and the specific absorption ($E^{1\%}_{1\,cm}$) of the substance to be determined. P. HAAS

3185. **Quantitative polarographic determination of chlorophyll in dentifrice by a "quantitative bridge".** Sachio Kondo and Itsuhiko Mori (Sun-star Dentifrice Co. Ltd., Shijo, Tatsumi-cho, Nakagawachi-gun, Osaka). *J. Pharm. Soc. Japan*, 1955, **75** (5), 519–520.—The use of a "quantitative bridge" (*cf.* Mori, *Anal. Abstr.*, 1954, **1**, 2606) for the determination of chlorophyll (**I**) was studied with a mixture of butanol, ethanol and NH_4Cl (1 per cent.) (2:1:1). Two parallel lines (2 mm apart, both 60 mm long) are slit with a sharp blade on chromatographic paper; melted paraffin wax is smeared outside the slits so that the soln. can ascend only through the narrow bridge ("quantitative bridge"). Tooth paste or powder (10 to 30 mg) is dissolved in 6 *N* HCl and extracted with ether (10 to 20 ml); the ether layer is evaporated to dryness and dissolved in butanol (1 ml). This soln. is spotted at a point 60 mm from one end of the bridge and developed at 25° C. The log. of the length (5 to 10 mm) of the green pattern on the bridge is proportional to the concn. of **I** (2 to 20 μg per ml). The overall error of determination is $\simeq$ 4·5 per cent. K. SAITO

See also Abstracts 2947, 2956, 3016, 3104, 3133, 3138, 3139, 3187, 3230.

Food

3186. **Further results on moisture determination of foods by hydrogen nuclei magnetic resonance.** R. H. Elsken and C. H. Kunsman (U.S. Dept. Agric., Albany, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 434–444.—In the determination of water by the nuclear magnetic resonance method (based on observation of the electromagnetic effects accompanying the reorientation of magnetic moments under specified conditions), only one absorption band, that of the hydrogen nuclei, is utilised. The method is satisfactory in the absence of an appreciable quantity of soluble solids, the hydrogen nuclei of which also absorb energy. If the amount of soluble solids is small and constant, a calibration curve can be constructed to relate moisture content with nuclear magnetic resonance absorption. For potatoes, more than 90 per cent. of the measurements agreed with vacuum-oven determinations to within $\pm$ 2 per cent. The standard deviation was 1·2 per cent. The standard deviation for apples, 7·7 per cent., was reduced to 1·3 per cent. by applying a correction for the average percentage of soluble solids. A. A. ELDRIDGE

3187. **Micro-determination of iodine in dietary foods, vitamin - mineral preparations, and drugs.** D. Menschenfreund (Food & Drug Admin., Dept. of Health, Educ. and Welfare, Los Angeles, Calif., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 523–528.—The powdered sample ($\equiv$ 0·03 to 0·1 mg of I) is heated with ethanolic KOH, dried, charred and ashed. The ash is leached with water and the filtered extract, after acidification with H_2SO_4, is rendered alkaline (pH 8) with NaOH. It is then boiled, oxidised with $KMnO_4$, filtered, brought to pH 8, and then treated with xylene, KI solution and (dropwise) HCl. After shaking, the aqueous layer is again extracted with xylene. The extinction of the xylene solution is measured at 494 mμ. With one tablet containing 0·018 to 0·090 mg of I or two tablets containing 0·038 to 0·173 mg of I, consistent recoveries of approx. 100 per cent. were obtained in comparison with the official (A.O.A.C.) method in which 10 to 30 tablets are used. A. A. ELDRIDGE

3188. **New gasometric method for the estimation of sugars by fermentation in the presence of 2:4-dinitrophenol.** K. Beran and M. Burger (Biol. Inst., Czech. Acad. Sci., Prague, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1956, **21** (2), 405–411.—Approximately quant. estimations of glucose and maltose are made by measuring the CO_2 produced by fermenting the sugars with yeast in the presence of 2:4-dinitrophenol. When *Saccharomyces cerevisiae* is the yeast employed, the optimum concn. of 2:4-dinitrophenol is $7{\cdot}5 \times 10^{-5}$ *M*. A new form of fermentometer is described that simplifies the procedure and reduces the time of the analysis. J. H. WATON

3189. **Determination of water in molasses.** P. Honig and L. Sattler. *Int. Sugar J.*, 1956, **58**, 92–95.—The differences between results obtained by the Karl Fischer method and two statistically examined vacuum-drying methods are discussed. There was little difference in accuracy between the two vacuum methods (a standard method in which diluted molasses was absorbed on asbestos and a smear method with the use of microscope slides), except that it was not always possible to obtain a representative sample by the latter method. The

Karl Fischer method gave higher values (up to 2·5 per cent. more) than those given by the more accurate vacuum methods. This may have been due to the reaction of the reagent with organic non-sugars or water of hydration in addition to free water. The Karl Fischer method is not recommended for the determination of water in molasses. SUGAR INDUSTRY ABSTR.

3190. **Glass colour-standards for maple syrup.** B. A. Brice and A. Turner, jun. (Eastern Regional Res. Lab., U.S. Dept. of Agric., Philadelphia, U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (4), 293–299.—Earlier colour standards adopted by the U.S. Dept. of Agriculture for assessing the colour grading of maple syrup were solutions of sugar caramel in glycerol. These solutions exhibited slight fading on exposure to light and were difficult to duplicate exactly if different batches of commercial granulated sugar were used for preparation of the caramel. Glass colour-standards, and an improved colour comparator, have now been developed. Complete colour characteristics of the old standard solutions and the new glass standards have now been investigated and specifications established. B. S. COOPER

3191. **Impurities in starch syrups.** E. Lindemann. *Stärke*, 1956, **8**, 1–4.—Colorimetric methods for the determination of trace amounts of three impurities present in starch syrups are given in detail. *Determination of proteins*—A 4-g sample is decomposed with H_2SO_4 (Kjeldahl) and the ammonia distilled off is estimated with Nessler reagent at 430 mμ. The protein content of commercial syrups was found to be 0·01 to 0·07 per cent. *Determination of copper*—A 3-g sample is digested with H_2SO_4 and HNO_3; when the solution is clear, it is neutralised with ammonia. The copper is then determined with diethyldithiocarbamate dissolved in *iso*amyl acetate. Commercial syrups were found to contain 0 to 5 mg of Cu per kg. *Determination of iron*—Hänni's method (*cf. Brit. Abstr. C*, 1953, 223) is used, with *o*-phenanthroline. The iron content of commercial syrups was found to be 0 to 3 mg per kg. E. DUX

3192. **Determination of dialdehyde units in periodate-oxidised corn starches.** J. C. Rankin and C. L. Mehltretter (N. Utilisation Res. Branch, Peoria, Ill., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1012–1014.—Two methods are described. The first involves reduction of the dialdehyde groups with sodium borohydride; the difference between H evolved from the hydrolysis of a blank solution of sodium borohydride and of a mixture after the reaction of the reagent with the oxystarch sample gives a measure of the reduction of the carbonyl groups in the dialdehyde units of oxystarch. The second method involves the oxidation of the oxystarch with sodium periodate and measurement of the sodium periodate consumed. The results of both methods agree within 4·0 per cent., the standard deviations being $\simeq \pm$ 1·0 per cent. at the 95, 62 and 12 per cent. dialdehyde levels in oxystarch. The accuracy is also good. G. P. COOK

3193. **A tentative method for the determination of the grade strength of agars.** N. R. Jones (British Food Manufacturing Industries Res. Ass., Leatherhead, England). *Analyst*, 1956, **81**, 243–244.—The proposed method depends on the determination of the percentage of agar required to produce a jelly of a given strength when prepared under standard conditions. The standard strength chosen is 75 g for a deflection of 20° on the F.I.R.A. jelly tester. The tests are made at two concn. of agar (0·5 and 1 per cent.), and the concn. required to produce a jelly of standard strength is found by interpolation. A. O. JONES

3194. **Some physical properties of milk. II. Effects of age upon the viscosity of pasteurised whole milk.** C. H. Witnah, W. D. Rutz and H. C. Fryer (Kansas State Coll., Manhattan, U.S.A.). *J. Dairy Sci.*, 1956, **39** (4), 356–363.—The increase in viscosity of both homogenised and non-homogenised pasteurised milk as a result of storage of the milk at 4° C, measured at temp. between 4° and 44° C, is found to be an approximately linear function of the log. of the storage time. Methods are detailed for preparing charts from which the viscosity of milk containing known amounts of fat and total solids, and which has received a standard pasteurisation treatment, can be estimated for any storage period up to 300 hr. from the observed viscosity after a known period. Details are given of a modified Ostwald viscometer for carrying out the determinations and of the precautions necessary to obtain reproducible results. W. H. C. SHAW

3195. **A plan for the rapid determination of the major cations in milk.** G. K. Murthy and R. McL. Whitney (Illinois Univ., Urbana, Ill., U.S.A.). *J. Dairy Sci.*, 1956, **39** (4), 364–373.—By the flame-photometric methods described, $Na^{\cdot}$, $K^{\cdot}$ and $Ca^{\cdot\cdot}$ in milk can be determined with standard deviations of $\pm$0·70, $\pm$0·42 and $\pm$0·33 per cent., respectively; the Mg is calculated from the sum of Ca and Mg, determined by EDTA titration, corrected for $Ca^{\cdot\cdot}$. The sample is prepared for the assay by the preliminary removal of $PO_4^{\prime\prime\prime}$ on anion-exchange resin. The results obtained agree well with those given by an ashing method. *Procedure*—Use deionised water throughout. Dilute 10 ml of milk sample with 20 ml of water, add 2 ml of *N* HCl, stir and set aside for 10 minutes. Adjust to a pH of 4·0 to 4·1 with 0·5 *N* aq. NH_3, transfer to a 100-ml flask, dilute to vol. with water, mix and filter through a Whatman No. 42 filter-paper. Shake mechanically 30 ml of clear filtrate with 15 g of resin (Nalcite SAR), in the chloride form, for 15 minutes. Filter through a No. 42 paper into a 100-ml flask, wash the resin and filter three times with 20-ml quantities of water and dilute the filtrate to vol. with water. The resin is prepared by washing three times with 2·5 times its weight of deionised water and drying on blotting paper. Standard solutions for flame photometry are prepared from NaCl and KCl and from $CaCO_3$ dissolved in the minimum of HCl. Lactose, NH_4Cl and DL-alanine are included in all standards to simulate milk serum and LiCl is used as internal standard. The sum of Ca and Mg is determined in the resin-treated sample by the method of Jenners (*Brit. Abstr. C*, 1953, 439). W. H. C. SHAW

3196. **A hydroxamate method for characterising milk fat.** R. Bassette and M. Keeney (Dairy Dept., Univ. of Md., College Park, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 469–475.—Characterisation of milk fat is based on the reaction between organic esters and hydroxylamine under alkaline conditions, whereby hydroxamic acid derivatives of the corresponding organic acids are formed; these substances form coloured complexes with $Fe^{\cdot\cdot\cdot}$ in

acid media and may be determined spectrophotometrically. The melted fat (0·1 g), mixed with hydroxylamine hydrochloride solution and then a solution of KOH in *iso*propyl alcohol, is kept at 30° C for 30 min., the mixture being then shaken with acetic acid - chloroform solution and clarified with glass wool. One portion is shaken with acetone, chloroform and water, and an aliquot part of the aqueous layer is removed and diluted with *iso*propyl alcohol. Two other, smaller, portions of the acidified reaction mixture are diluted with acetone, *iso*propyl alcohol and water. On mixing all three samples with acidified $FeCl_3$ solution the same intensity of red colour is developed if the original sample was pure milk fat. When no milk fat is present the "aqueous" sample exhibits no red colour. By measurement in a photo-electric colorimeter, the hydroxamic acid index, which is approximately equivalent to the mol. percentage of water-soluble fatty acids in the fat, can be calculated. The method gives reproducible results with a correlation coefficient of 0·88 with the butyric acid content. A. A. ELDRIDGE

3197. **A rapid silica gel method for measuring total free fatty acids in milk.** W. J. Harper, D. P. Schwartz and I. S. El-Hagarawy (Ohio State Univ., Columbus, U.S.A.). *J. Dairy Sci.*, 1956, **39** (1), 46–50.—The chromatographic procedure of Harper and Armstrong (*Anal. Abstr.*, 1954, **1**, 2535) for the separate determination of butyric and higher fatty acids is modified so as to permit the elution of all free fatty acids from the two-section silica columns with 150 ml of chloroform - *n*-butanol (19:1). The method, which requires 5 to 20 g of sample, is rapid and gives quant. recovery of added fatty acids. The results obtained are compared with those given by the earlier procedure (*loc. cit.*) and by a solvent-extraction method; the differences found are discussed. W. H. C. SHAW

3198. **Use of sequestering agents to solubilise proteins in the determination of extraneous materials in foods by direct filtration methods.** M. G. Yakowitz (Div. of Microbiol., Food & Drug Admin., Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 532–533.—Cheese is soaked in water at 33° to 40° C for 30 min., and the stirred mixture is maintained at pH 7·5 with Na_3PO_4 for 2 hr. while pancreatin extract is added. The mixture is kept at pH 7 with HCl while Cheelox B-14 (a solution of soluble salts of aminocarboxylic acids) is added. Then, after dilution, a surface-active preparation (Igepon TK-32) is added and the mixture is filtered, with alcohol in the suction flask to control foam. A. A. ELDRIDGE

3199. **Determination of added distinctive cations in whisky. III. Flame-spectrophotometric determination of caesium and rubidium.** M. J. Pro, R. A. Nelson and A. P. Mathers (Alcohol and Tobacco Tax Div. Lab., Internal Revenue Service, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 506–512.—Flame spectrophotometry affords the most satisfactory method for determining traces of Cs and Rb added to whisky for the purpose of identifying brands. The technique is detailed. Both metals can be determined with precision and accuracy in the presence of a large excess of K and Na (which enhance the emission) by the use of standard solutions of Cs and Rb, respectively, which contain also K and Na in the concentrations found in whisky. Other cations studied, and chlorides, nitrates and sulphates (< 1000 p.p.m.), had no effect; phosphate (> 200 p.p.m.) and perchlorate (> 50,000 p.p.m.) reduce the intensity of light emission. A. A. ELDRIDGE

3200. **Chromatographic separation of fatty acids for analytical purposes.** W. Kapitel (Henkel u. Cie, Düsseldorf, Germany). *Fette u. Seifen*, 1956, **58** (2), 91–94.—A method is described for the quant. separation of natural saturated fatty acids containing 6 to 22 carbon atoms. A 3-mg sample of the mixture is deposited on a column of kieselguhr, treated with dimethyldichlorosilane and saturated with liquid paraffin; the column is maintained at 35° C, and the acids are eluted with mixtures of acetone and water saturated with paraffin, the proportion of acetone in the eluent being gradually increased as the separation proceeds. Oleic, linoleic and linolenic acids can be separated from one another and from stearic acid, but oleic cannot be separated from palmitic acid. The unsaturated C_{18} acids cannot be separated satisfactorily from palmitic and myristic acids, and mixtures containing unsaturated acids must be hydrogenated before chromatography. The method can also be used for the separation of fatty alcohols; the elution of these is followed by oxidising the eluted fractions with CrO_3 (half the theoretical quantity) in acetic acid and determining the acid formed. Hydroxy acids move rapidly and are easily separated from other fatty acids. E. HAYES

3201. **The identification and determination of vitamin A and β-carotene in an animal-fat mixture.** J. Gillman, K. B. Norton, D. E. A. Rivett and D. A. Sutton (Joint Nutrition Unit, S.A. Council for Sci. and Ind. Res., Univ. of Witwatersrand, Johannesburg). *Biochem. J.*, 1956, **63** (3), 458–460.—A chemical assay of vitamin A in a mixture of beef fat and mutton fat is described. *Procedure*—Saponify the fat (50 g) by the method of Boldingh and Drost (*Brit. Abstr. C*, 1952, 113), and treat the ethanolic soln. with cold water until the alcohol content is approx. 35 per cent. v/v. Extract with peroxide-free ether (1 × 500 ml; 2 × 250 ml), wash the combined extracts with boiled distilled water (5 × 30 ml), and evaporate the ether. All these processes are carried out in N and in the presence of a little quinol. Remove water from the residue under a water-pump vacuum at room temp. Dissolve the residue (≃ 0·16 g) in dry ether (5 ml) and add dry hexane (15 ml). Keep the solution for 30 min. so that the cholesterol can crystallise. Chromatograph a portion (2 ml) of the solution on Al_2O_3 (heated at 105° C for 3 hr.) by the method of Thompson *et al.* (*Brit. Abstr. AIII*, 1950, 745), and determine the vitamin-A content of the eluate (after evaporation in N) by the Carr - Price method. J. N. ASHLEY

3202. **Slope-ratio liver-storage bioassay for vitamin A.** S. R. Ames and P. L. Harris (Dist. Prod. Ind., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 874–878.—The method used depends on a "5-point common-zero" statistical design, in which four groups of rats, depleted of measurable liver vitamin-A reserves, are supplemented with two levels of reference standard and two similar levels of test material, the fifth group being a negative control. The relative potency is determined by the ratio of the slopes of the two linear dose - response curves. The response is

linear over a dose-range of 500 to 10,000 units. The vitamin A was determined by the method of Ames, Risley and Harris (*Anal. Abstr.*, 1954, **1**, 3126). When the U.S.P. reference standard was fed, 67 per cent. of the vitamin A was found in the liver. G. P. Cook

3203. **Quantitative estimation of vitamins D_2 and D_3 in pure solution.** D. H. Laughland and W. E. J. Phillips (Dept. Agric., Ottawa, Ont., Canada). *Anal. Chem.*, 1956, **28** (5), 817–819.—The method is based on the formation of a coloured reaction product when the vitamins D are treated with furfuraldehyde and H_2SO_4 under carefully controlled conditions. Distinctive absorption curves are obtained for the two forms of the vitamin, and binary mixtures can be analysed by differential spectrophotometry at two wavelengths. As little as 15 μg of total vitamin D can be estimated. G. P. Cook

3204. **Fluorimetric determination of thiamine and riboflavine in mixtures.** W. E. Ohnesorge and L. B. Rogers (M.I.T., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (6), 1017–1021.—Thiamine is measured by oxidation to thiochrome, which is measured fluorimetrically under u.v. light. Riboflavine is measured directly. Mixtures of the two vitamins are determined by differential measurement of the fluorescence at 450 mμ (thiochrome) and 530 mμ (riboflavine), light of 365 mμ being used for excitation. The concn. range is 0·5 to 4·0 p.p.m., with a standard deviation of $\simeq \pm$ 5·0 per cent. for each compound. Recoveries from synthetic samples were $>$ 90 per cent. G. P. Cook

3205. **A vitamin-B_{12} binding substance obtained from *Lactobacillus leichmannii* 7830.** E. M. Stapert, J. W. Goff and L. Stubberfield (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (5), 309–311.—A substance that binds vitamin B_{12} and inhibits the growth of the *Lb. leichmannii* 7830 organism (**I**) is present in the medium in which **I** has been cultured, and can be extracted from cells of **I**. Extracts of used medium or of cells retain their activity after being filtered through a Selas candle, adsorbed on charcoal and freeze-dried. Inhibition of growth caused by this substance can be prevented by autoclaving in the presence of the medium. A. R. Rogers

See also Abstracts 2982, 3086, 3137.

Sanitation

3206. **Ferric thiocyanate paper as analytical reagent for testing air.** W. Deckert (Hygienisches Inst., Hamburg). *Z. anal. Chem.*, 1956, **150** (6), 421–425.—Paper strips impregnated with $Fe(SCN)_3$ ($\simeq$ 4 mg of Fe^{III} for 50 sq. cm of paper) are used for the quant. evaluation of air pollution by gases with alkaline reaction (NH_3, amines, ethylene oxide). These gases decolorise the paper. For 1 litre of air aspirated over the paper, the lower limit of sensitivity is 0·07 μg of NH_3. Such paper is useful for testing air near fish-meal factories and particularly for evaluating the efficacy of scrubbers and air-purification plant. When first decolorised by NH_3, the paper can also be used as a sensitive test for acidic gases (development of red colour). *Procedure*—Immerse chromatographic paper (1 cm $\times \simeq$ 7 cm) in a mixture of 96 ml of 40 per cent. KSCN soln. and 4 ml of 10 per cent. $FeNH_4(SO_4)_2$ for 1 to 2 sec. Then let the paper dry in clean moist air at $<$ 20° C. Determine the content of Fe (if necessary) by elution with HCl and colorimetry. In use let only the leading edge of the paper be decolorised so as to facilitate evaluation of the amount of gas reacted. J. P. Stern

3207. **Infra-red spectrometric method for monitoring gaseous organic substances in the atmosphere.** F. E. Littman and J. Q. Denton (Air Research Lab., Pasadena, Calif., U.S.A.).—*Anal. Chem.*, 1956, **28** (6), 945–949.—A non-dispersive i.r. gas-analyser for continuously recording changes in concn. (0·1 to 10 p.p.m.) of gaseous organic substances in the air is described. The instrument has a response time of $\simeq$ 1 min. and is sensitive to 1 p.p.m. of butane per 7·2 scale divisions. No initial treatment of the air is necessary. Unless the composition of the organic compound(s) is known, the observed concn. are expressed in terms of butane. Interference by CO and CO_2 is eliminated completely by filling the filter cells (290 cm) with a mixture of CO_2 and CO (4 + 1). The mean sensitivities to different paraffins, olefins, aldehydes and ketones are listed. W. J. Baker

3208. **Determination of radioactive strontium and barium in water.** R. B. Hahn and C. P. Straub. *J. Amer. Wat. Wks Ass.*, 1955, **47**, 335–340.—A procedure has been evolved for the determination of radioactive Sr and Ba in low concn. such as would be encountered in public water supplies contaminated by radioactive materials. Methods of concentrating the active isotopes are evaluated and concn. by pptn. is considered to be most suitable for the relatively large vol. of sample required. Full details of the determination of Sr and Ba activities to levels of about 4×10^{-8} μC per ml and 10^{-7} μC per ml, respectively, are given in an appendix. The method was tested on various radioactively charged natural and waste waters, and a precision of about 10 per cent. was obtained. Water Pollution Abstr.

3209. **The storage of sea-water samples for the determination of dissolved inorganic phosphate.** J. Murphy and J. P. Riley (Liverpool Univ., England). *Anal. Chim. Acta*, 1956, **14** (4), 318–319.—Samples should be filtered, and then stored in the dark after the addition of chloroform (0·7 ml per 100 ml of sample). Polyethylene bottles must not be used since these adsorb phosphate ion. C. A. Slater

3210. **Continuous measurement of the salinity of sea water by means of a high-frequency apparatus.** Sôichrô Musha, Makoto Munemori, Mitsuo Ito, Masami Takeda, Shôichirô Nakamura, Etsuo Inoue, Takeo Kawamoto and Hiroyuki Kitamura (Faculty of Eng., Osaka Prefectural Univ., Sakai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (1), 140–144.—The high-frequency apparatus for measurement of the concn. of electrolytes (a kind of high-frequency conductometer) devised by one of the authors (Musha *et al.*, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1955, **58**, 482) was used to measure the salinity of sea water. The correlation between the chlorinity and the concn. of salt measured by the present method is discussed. It appears to be desirable to compensate the temp. factor by a servo-mechanism so that the reading of the high-frequency apparatus directly indicates the salinity. K. Saito

3211. **Thiocyanate estimation of phosphate in boiler water.** L. Pika (Hradec Trálové ČSR). *Chem. Tech., Berlin*, 1956, **8** (1), 45.—The new volumetric method described is based on the pptn. of the PO_4''' as Ag_3PO_4 by $AgNO_3$ in presence of chlorides (NaCl) in weak acetic acid solution, selectively dissolving the Ag_3PO_4 from the ppt. with dilute H_2SO_4, and titrating the $Ag^{\cdot}$ in the resulting solution with KSCN solution, with a Fe^{III} indicator. The presence of chloride enables complete pptn. of the PO_4''' as Ag_3PO_4 to be effected and produces a readily filterable ppt. *Procedure*—The sample (200 ml) is neutralised with 0·1 *N* H_2SO_4 (methyl red indicator), then $\simeq$ 1·5 g of powdered Na acetate, 10 ml of 0·2 *N* NaCl and 10 ml of 0·1 *N* $AgNO_3$ are added and the mixture is warmed till the ppt. of AgCl and Ag_3PO_4 packs together. The ppt. is washed successively with water, dil. H_2SO_4 and water. The resulting Ag_2SO_4 solution is collected and, after adding 1 ml of $Fe_2(SO_4)_3$ solution, is titrated to a red end-point with 0·02 *N* KSCN solution from a micro-burette. The results are markedly different from those of the usual gravimetric and photometric (Mo colorimetric) methods, but are more accurate, since there is less interference by foreign ions.

H. L. Whitehead

3212. **Recommended methods for the analysis of trade effluents. Methods for the determination of iron, mercury and nickel.** Joint A.B.C.M. - S.A.C. Committee on methods for the analysis of trade effluents. *Analyst*, 1956, **81**, 176-180.—After destruction of organic matter, Fe is determined colorimetrically as the purple thioglycollate, either spectrophotometrically at 490 mμ or visually in Nessler cylinders against standard soln. In the determination of Hg, organic matter is destroyed by a special method (treatment with HNO_3 - $KMnO_4$ under pressure), Fe is suppressed by hydroxylamine, the soln. is acidified to eliminate other heavy metals and the Hg is extracted with toluene as the golden-brown dithizonate. This soln. is then examined spectrophotometrically at 480 mμ or absorptiometrically with a suitable blue filter. Nickel is determined, after destruction of organic matter, by extraction with chloroform from ammoniacal soln. as its dimethylglyoxime complex. The Ni is extracted from the chloroform with HCl, oxidised to the nickelic glyoxime complex, which is then determined spectrophotometrically at 480 mμ, absorptiometrically or visually.

A. O. Jones

3213. **Effect of synthetic detergents on B.O.D. test.** W. D. Sheets and G. W. Malaney. *Bull. Ohio Engng Exp. Sta. No.* 157, 1955, **24** (3), 1–10.—An investigation was carried out on the influence of synthetic detergents, surface-active agents and detergent builders on the standard dilution B.O.D. test, with synthetic sewage. The various materials used are listed and their chemical nature given. The technique of testing is described and the results are discussed. It is shown that anionic detergents increased the apparent B.O.D. in varying degrees; that cationic detergents had an inhibitory effect on B.O.D. to a marked extent and non-ionic detergents to a less extent; and that cationic detergents exhibited an iodine demand in concn. of 10 p.p.m. and above. Changes in oxygen depletion by added increments of detergents and the neutralisation of inhibitory effects of cationic by anionic detergents are shown graphically. The allowance to be made for the effect of synthetic detergents on B.O.D. tests in studies of their influence on specific sewage-treatment processes is discussed. Water Pollution Abstr.

See also Abstracts 2955, 3042.

Agriculture and Plant Biochemistry

3214. **Determination of trace elements in agricultural chemistry.** H. Schüller (Landwirtsch.-chem. Bundesversuchanstalt, Vienna). *Mikrochim. Acta*, 1956, (1–3), 393–400.—A method is described for the determination of the trace elements Mn, Cu, Zn, Ni, Co and V in soils, plants, feeding-stuffs and fertilisers. The trace elements are separated from 100-g samples with ammonium acetate soln.; they are then concentrated by shaking with complex-forming reagents following the techniques of Mitchell. The organic material is destroyed and the ashed concentrate is dissolved in 1 ml of HCl. This soln. is continuously absorbed on to the underside of a pure carbon rotating disc (10 mm in diam.) whilst being simultaneously excited with a normal type of spark discharge using a pure carbon counter-electrode. Iron is added as internal comparison element. An optical filter having step transmissions of 10 per cent. and 100 per cent. permits measurement of high-density lines. The following line-pairs are used: Mn 2933, 2939, 2949 - Fe 2948; V 3102, 3185 - Fe 3226; Cu 3247 - Fe 3226; Zn 3345 - Fe 3407; Co 3405, 3453 - Fe 3407, 3444; Ni 3415 - Fe 3407. Calibration is made against standards of known contents. Recoveries of added elements are shown to be satisfactory over the range 1 to 1000 p.p.m. Should the content of Mn exceed 5000 p.p.m., simultaneous determination of this element is not possible. It can either be determined on a separate aliquot from the extract or colorimetrically determined. In cases of such high Mn content, calibration soln. should contain a corresponding Mn concn. D. F. Phillips

3215. **New findings on the micro-determination of phosphates and their application to the determination of the most easily soluble phosphates in soils.** C. Ferrari (Inst. Chem. Agric., Univ. Bologna, Italy). *Mikrochim. Acta*, 1956, (1–3), 551–564.—Extensive details are given of a new method for determining the most easily soluble phosphates in soils, which is being used extensively in Italy for assessing the phosphate fertility. In this method the molybdophosphate blue is developed in the presence of the soil itself and not in an extract in order to avoid the development of equilibria between phosphate ions present in the solution and those retained in the soil itself. D. F. Phillips

3216. **Colorimetric determination of nitrofurazone and furazolidone in feeds and premixes.** J. A. Buzard, V. R. Ells and M. F. Paul (Norwich Pharmacal Co., Norwich, N.Y., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 512–518.—Nitrofurazone (5-nitro-2-furfuraldehyde semicarbazone) and furazolidone [3-(5-nitro-2-furfurylidene-amino-2-oxazolidone] are converted into 5-nitrofurfuraldehyde phenylhydrazone by extraction with ethanol and treatment with phenylhydrazine hydrochloride and HCl. The extinction of the red colour is measured with a photo-electric colorimeter. The method gives reproducible results; recoveries of 91·0 to 104·5 per cent. of added furazolidone and 92·9 to 101·9 per cent. of added nitrofurazone are reported. Many other substances

likely to be found in poultry feeding-stuffs have been shown not to interfere. A. A. ELDRIDGE

3217. **Qualitative tests for rapid identification of chlorinated hydrocarbons in insecticide formulations.** D. P. Johnson (N.C. Dept. Agric., Raleigh, U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 490–497.—The selected tests, which are designed primarily for dusts, may also be applied directly to liquid preparations in small volume; but if the percentage of insecticide in the liquid is small, preliminary isolation by partition chromatography may be necessary. Rapid qual. tests for detecting and identifying the following substances are described—chlordane, methoxychlor, toxaphene, DDD [dichlorodi(chlorophenyl)ethane], DDD in the presence of methoxychlor, DDT, heptachlor, aldrin, dieldrin and endrin. A. A. ELDRIDGE

3218. **Separation and identification of chlorinated organic pesticides by paper chromatography. VII. Aramite, captan, dieldrin, lindane, Spergon and tritisan.** L. C. Mitchell (Food and Drug Admin., Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1956, **39** (2), 484–489.—Aramite (1-*p*-*tert*.-butylphenoxy-2-propyl 2-choloroethyl sulphite), captan (N-trichloromethylthio-4-*cyclo*hexene-1:2-dicarboxyimide), dieldrin, lindane, Spergon (chloranil) and tritisan (pentachloronitrobenzene) can be separated and identified by a paper-chromatographic technique. One set of spotted papers is sprayed with acetic anhydride in ether and developed with *n*-heptane. Another set is sprayed with soya-bean oil in ether and developed with ethanol. When dry, one paper from each of the two tanks is treated as follows: spray with aq. $AgNO_3$, dry; spray with aq. glycerol and KOH, heat for 30 to 45 min. at 160° to 165° C, cool; spray with HNO_3 and H_2O_2, wash after 30 min., dry; expose to u.v. light. The second chromatogram is treated as follows: spray with alcoholic ammoniacal $AgNO_3$, dry; expose to u.v. light; spray with pyrogallol in ethanol, dry. Figures illustrating the separations achieved are presented. A. A. ELDRIDGE

See also Abstracts 2951, 2979, 3090.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

3219. **Inexpensive micro vacuum-desiccator.** C. G. Skinner (Univ. of Texas, Austin, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 924.—A simple vaccum-desiccator (17 cm × 4·6 cm) to hold sintered-glass crucibles or sample bottles is described. By fitting five such desiccators into holes bored in a wood block (14 in. × 3 in. × 3 in.), five separate materials (P_2O_5, H_2SO_4, KOH, $CaSO_4$ and liquid paraffin) are immediately available, *e.g.*, for the removal of an excess of solvent from recrystallised solids. W. J. BAKER

3220. **A pipette for taking blood with exclusion of air for blood-gas analysis.** R. Dittmeyer and A. Wallner (Univ. Frauenklinik, Erlangen, Germany). *Klin. Wochschr.*, 1956, **34** (21–22), 601–602.—The blood is drawn directly from a vein or artery into a mixing chamber filled with a suitable diluent; the vol. of blood is measured by the amount of fluid displaced into another chamber connected to the mixing chamber by a three-way tap. A measured vol. of the mixed diluted blood can be transferred directly to the gas-analysis apparatus through an outlet tube also connected to the mixing chamber by the three-way tap. H. F. W. KIRKPATRICK

See also Abstracts 3107, 3117.

Optical

3221. **X-ray absorptiometer for the determination of tetraethyl-lead in petrol.** J. F. Brown and R. J. Weir (I.C.I., Billingham, England). *J. Sci. Instrum.*, 1956, **33** (6), 222–225.—Constructional details and circuit diagrams are given. The apparatus is capable of determining the tetraethyl-lead content of petrol over the range 0 to 1·5 ml per litre with an accuracy of ± 0·005 ml per litre. G. SKIRROW

3222. **Spectrophotometric measurements on minimum liquid volumes.** G. Hansen (Oberkochen, Germany). *Mikrochim. Acta*, 1956, (1-3), 406–413.—Investigations into the optimum conditions for obtaining maximum precision of spectrophotometric measurements with minimum sample volumes are described. The volume of all cells which permit the passage of a given light flux is proportional to (cell length)^2. With filter photometers the proportionality factor is solely dependent on the light source and receiver characteristics; with a monochromator, also on the dimensions and resolving power of the monochromator. With the Zeiss spectrophotometer PMQ II, in the green region, it is possible to use a volume <0·1 ml without loss of precision. D. F. PHILLIPS

3223. **Equipment for high-pressure optical and spectroscopic studies.** E. Fishman and H. G. Drickamer (Univ. of Ill., Urbana, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 804–806.—A combined intensifier and spectroscopic bomb for making optical and spectroscopic measurements in liquids at pressures up to 12,000 atm. is described. Synthetic sapphire windows enable measurements to be made at wavelengths from 0·2 to 5 μ. A source assembly for use with a single-beam spectrometer is also described. The effects of pressure on refractive index and on light-scatter or absorption, *e.g.*, in polymer soln., can also be studied with the equipment. W. J. BAKER

3224. **Vacuum spectroscopy.** E. Lüscher (École Polytech., University, Lausanne, Switzerland). *Chimia (Switz.)*, 1955, **9**, 298–302.—A brief survey of vacuum spectroscopy is given. The technique might well be applied to the analysis of C, P and S in steel. By using spectral lines in the regions 180 to 200 mμ or 90 to 100 mμ, these elements can be determined with a sensitivity of 0·01 per cent. for C and 0·005 per cent. for P and S. J. H. WATON

3225. **Quantitative spectrochemical analysis by flame photometry. IV. Temperature measurement of flame sources by means of reversal of resonance line (Na D line).** Ryohei Ishida (Gov. Chem. Ind. Res. Inst., Hatagaya, Yoyogi, Tokyo). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (2), 238–241.—The temp. of flames of various burners, including those that use propane - air (1830° C), acetylene - air (2165° C), acetylene - oxygen (2497° C) and hydrogen - oxygen (2168° C), were measured by means of reversal of the Na_D line. Visible

light from a filament source is introduced into a spectrophotometer through the flame with the aid of two lenses. When the brightness temp. of the source is equal to that of the flame, neither absorption nor emission can be observed on the spectrogram. The brightness of the source with varying electric current was calibrated with standard lamps. It was found that the temp. of a flame is dependent not only on the composition and rate of flow of the fuel gas, but also on the geometry of small holes of the burner, from which gas flows.

V. The CaF band-spectrum. Ryohei Ishida. *Ibid.*, 1956, **77** (2), 241–242.—The use of a flame source for excitation of the CaF band-spectrum was studied with burners of various temp. An appreciable band for CaF (5291 A) was observed on a photographic plate only when an acetylene-oxygen burner (2500° C) was used. The limit of detection is $\simeq$ 300 p.p.m. of NaF soln. in the presence of $CaCl_2$ (20 per cent., one-fifth of the vol. of the sample soln.).

VI. The sensitivity of various spectral lines in flames. Ryohei Ishida. *Ibid.*, 1956, **77** (2), 242-244.—The relationship between intensities of various lines and the rate of flow of the fuel gas (acetylene) was studied for alkali and alkaline-earth metals. Each line shows a max. sensitivity at a certain pressure of acetylene, which is dependent on the wavelength irrespective of the nature of the line. The excitation potential of resonance lines which are generally used for flame-spectroscopic analysis decreases with increase in wavelength; there appears to be an overall trend towards a higher optimum temp. for excitation of a line with decrease in wavelength. K. SAITO

3226. **Effects that increase emission in flame photometry.** H. Siebert and S. Rapoport (Humboldt Univ., Berlin, Germany). *Z. anal. Chem.*, 1956, **150** (2), 81–93.—A systematic examination of the effect of various compounds on the intensity of emission of solutions of Na, K and Ca during flame photometry was carried out. The addition of salts of Na, K and Ca, as well as of organic compounds such as alcohols, ethanediol, glycerol, ethers, acetone, acetaldehyde and carboxylic acids, was studied and found generally to cause an increase in emission. A comparison of flame temperatures, viscosities and surface tension showed that these were not primarily responsible, and it is concluded that a genuine influence on the emission takes place. It is thought possible that radicles are formed from the added compounds, which act by direct excitation or by preventing interference of radicles normally present in the flame. New emission lines are found in the flame spectra as the concn. of the additives is increased. P. S. STROSS

3227. **Auxiliary recording system for the Perkin-Elmer model 21 spectrophotometer.** A. L. Olsen, D. J. Johnson and R. H. Pierson (U.S. Naval Ordnance Test Station, China Lake, Calif., U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (5), 354–358.—The auxiliary recording system described, designed on electronic principles, enables a reduced spectrum (8½ in. × 11 in. paper) to be recorded simultaneously with the main trace. The performance of the basic instrument is unaffected by this addition. A secondary time-base drive system has also been developed which enables the auxiliary recorder to be used for the recording of cyclic measurements of absorption phenomena. This feature enables the progress of reactions to be followed from a study of the succession of progressively altered traces of absorption peaks. B. S. COOPER

3228. **Automatic programmer for the Perkin-Elmer 21 infra-red spectrophotometer.** A. W. Baker, R. A. Crane, A. Opler and C. A. Diethelm (The Dow Chemical Co., Pittsburgh, Calif., U.S.A.). *Applied Spectroscopy*, 1956, **10** (2), 83–84.—A device is described which allows each of the 23 arbitrary intervals of 0·6 μ between 2·0 and 15·8 μ to be scanned at any of five pre-selected speeds. Unwanted areas of the spectrum may thus be scanned over quickly, the important regions more slowly. Circuit details are given. P. T. BEALE

3229. **Simple device to control the atmosphere for arc spectroscopy.** J. W. Mellichamp (Signal Corps Engng Lab., Fort Monmouth, N.J., U.S.A.). *J. Opt. Soc. Amer.*, 1956, **46** (5), 359–360.—A small chamber, 2 in. in diam., 2 in. long, enables a normal spectrographic arc source to be run in a controlled atmosphere. The design was made with special reference to the stability of the arc and to ease of disassembly and cleaning between each burn. Gas enters the chamber so as to form a sheath round the lower, positive, electrode and escapes through an axial hole drilled through the cathode. Spectrograms illustrate the elimination of SiO bands through the use of an argon atmosphere. B. S. COOPER

3230. **A method of correcting for irrelevant absorption in ultra-violet spectrophotometric analysis.** G. C. Ashton and J. P. R. Tootill (Glaxo Lab. Ltd., Stoke Poges, Bucks., England). *Analyst*, 1956, **81**, 232–238.—Since the absorption spectra of impurities in extracts of griseofulvin follow a quadratic curve, the linear three-point correction of Morton and Stubbs cannot be applied and a seven-point correction procedure has been developed. The application of this correction procedure to samples of pure griseofulvin to which suitable impurities have been added is described. The results show that impurities with quadratic irrelevant absorption spectra can be accounted for, even when the amount of irrelevant absorption is two or three times that of the substance being analysed. The extension of the method to other types of irrelevant absorption is discussed, and also the loss of precision with increasing complexity of correction. A method for determining the degree of curvature (quadratic, cubic, etc.) of the irrelevant absorption spectrum is described. A. O. JONES

3231. **Derivative infra-red spectroscopy.** F. Singleton and G. Collier (R. Graesser Ltd., Sandycroft, nr. Chester, England). *Chem. & Ind.*, 1955, (47), 1519–1520.—An instrument for the production and measurement of second-derivative infra-red spectra $\frac{d^2I}{dt^2}$ has been used for qual. and quant. analysis. The function, $\frac{d^2I}{dt^2}$, produced by two successive differentiations of the spectrometer output when scanning at a fixed rate, is used to detect and fix the position of minor absorption (I) changes. Two per cent. of phenol was detected in commercial *o*-cresol in this way. Direct measurements of *m*-cresol in its commercial grades, carried out in < 10 min,, and by using a band resolved from a triplet at 10·7 μ, gave results that differed by 2 $\pm$ 0·6 per cent. from those obtained by the Tar Products Tests Committee nitration method. E. G. CUMMINS

3232. **The analytical application of reflectancy determination. V. Relation between reflectancy and amount of dye in spots on filter-paper.** Kazutaka Yamaguchi, Seizo Fukushima and Miyoko Ito (National Hyg. Lab., Tamagawa-Yoga, Setagaya-ku, Tokyo). *J. Pharm. Soc. Japan*, 1955, **75** (5), 556–559.—The empirical relationship between min. reflectance (R) (percentage) and the concn. of dye (c, mg per 100 ml) was studied on a filter-paper impregnated with various dyes for foodstuffs. When the value $(2 - \log R)$ is plotted against $\sqrt{c}$, an approx. linear diagram is obtained. A similar relation holds between R and the amount of dye-stuff in the spot. K. SAITO

See also Abstract 2960.

Thermal

3233. **A new Bunsen-type calorimeter.** R. S. Jessup (Nat. Bur. Stand., Washington, D.C., U.S.A.). *U.S. Bur. Stand. J. Res.*, 1955, **55** (6), 317–322.—The calorimeter described and sketched has a large central well to contain a reaction vessel when measuring small heats of reaction or of mixing, *e.g.*, of polymers and solvents; diphenyl ether (m.p. 26·87° C) is the calorimetric substance. The sensitivity is $\simeq$ 3·4 times that of the ice calorimeter, and when measuring amounts of heat $\equiv$ 38 g-cal. the accuracy is $\simeq$ 0·05 per cent. The method of forming a mantle of solid diphenyl ether over the central well does not completely obviate the entrapment of air in the solid, so that a new calibration should be made for each mantle. W. J. BAKER

3234. **An apparatus for the automatic determination of melting points.** P. Monand (Centre de Recherches de la Cie. Saint-Gobain). *Bull. Soc. Chim. France*, 1955, (11–12), 1601–1602.—Melting points are determined by placing the substance between a heated brass plate and a spring-loaded contact. When the substance melts, the contact touches the plate and operates a relay which switches off the current and lights a lamp or rings a bell. The m.p. is read on a max. thermometer inserted in a hole in the plate. E. J. H. BIRCH

3235. **Automatic control for fluoride distillation.** A. C. Kuyper (Wayne Univ. Coll. of Med., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 922.—The electrically operated thermoregulator described and illustrated controls the amount of gas delivered to the burner and maintains a const. temp. (to within $\pm$ 0·5° C) during steam-distillation (*e.g.*, of fluoride at 135° C for 1 or 2 hr.). The sensitivity of the control is based on the rapid rise in the v.p. of a liquid (ethanediol and water) as its b.p. is reached. W. J. BAKER

Electrical

3236. **Impedance method of zone localisation for paper chromatography which obviates the need for preliminary spraying.** G. G. Blake (Univ. Sydney, Australia). *Anal. Chim. Acta*, 1956, **14** (4), 329–335.—The radio-frequency zone locator described is based on the earlier application of radio-frequency currents to chemical analysis (*J. Sci. Instrum.*, 1947, **24**, 77). C. A. SLATER

3237. **Recording high-frequency paper chromatography.** F. Oehme (Inst. Microbiol. and Exp. Therap. Jena, Germany). *Z. anal. Chem.*, 1956, **150** (2), 93–99.—The apparatus described by Hashimoto and Mori (*J. Pharm. Soc. Japan*, 1952, **72**, 1532; *Z. anal. Chem.*, 1953, **140**, 286) has been adapted so that continuous recording of paper chromatograms is possible. The electrolyte-containing zones are detected by measuring changes inthe grid current of a quartz oscillator, a d.c. amplifier and pen recorder being used for recording. Semi-quantitative assessment is possible if the papers contain standardised amounts of moisture. The method was found to be applicable only to the detection of strong electrolytes; 10 μg of alkali-metal chlorides and 30 μg of sodium or ammonium acetate can be detected. P. S. STROSS

3238. **Concentration cell for following ion-exchange separation of halides.** L. P. Larson and H. C. Becker (The Texas Co., Beacon, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (5), 923.—In the Ag - AgCl concentration cell described the eluting soln. flows through one-half of the cell (before entering the column) and the eluate flows through the other half. The cell is simply a silver wire cemented in 8-mm glass tubing; the electrodes are given a coating of AgCl by electrolysis, and the half-cells are connected with a salt bridge of KNO_3 in agar. The cell potential gives only a semi-quant. measure of halide concn., but is sufficiently sensitive for the study of such factors as resin type, flow rates, column geometry and concn. and pH of the eluting soln. W. J. BAKER

3239. **Zone electrophoresis.** G. Dicastro (Medital Lab., Res. Div., Rome). *Bull. Soc. Chim. Belg.*, 1956, **65** (1–2), 97–102.—An apparatus is described for continuous electrophoresis, in which a Perspex box (24 cm × 32 cm × 2 cm), packed uniformly with cellulose powder, has perforations in the thin ends which communicate with electrode chambers into which dip electrodes of platinum wire wound on Perspex tubes. At the bottom of the box 16 small funnels drilled in a perspex block allow the fractions to be collected. Buffer is supplied separately to the cellulose powder and to the electrode compartments, in which it passes down the Perspex tube and overflows at the top providing a continuous washing of the electrode, so that no alteration of pH occurs with electrolysis. The material to be separated is introduced into the cellulose powder by a moveable wedge fed by a continuous automatic syringe. The apparatus was tested with mixtures of amino acids. E. J. H. BIRCH

3240. **An automatic device for quantitative estimate of paper electrophoresis and radio electrophoresis.** J. Sternberg (Inst. Microbiol. Hygiene, Univ. Montreal). *Mikrochim. Acta*, 1956, (1–3), 462–473.—A device is described which enables the simultaneous photometric scanning of paper electropherograms and radiometric assay of the protein spots to be carried out in $\simeq$ 2 hr. A photomultiplier is used to scan the stained paper which moves synchronously with a recording ammeter, and the intensity curve proportional to the transmittance is recorded in 1 to 2 min. Procedures for converting the direct graph to an interpretable form are described. Radioactive scanning is done by replacing the photomultiplier by a Geiger tube and the recorded trace is directly proportional to the real activity without reconversion. Applications are discussed. D. F. PHILLIPS

3241. **Modified method for measuring the wave height of the polarogram.** R. S. Subrahmanya (Indian Inst. Sci., Bangalore). *J. Indian Inst. Sci., A*, 1956, **38** (1), 26–32.—A number of improvements in technique are described which enable the

wave height of a polarogram to be determined from a photographic record, with an overall error of less than ± 0·5 per cent. A. JOBLING

3242. **A laboratory polarographic recorder for the determination of sulphur dioxide.** J. Gottfried (Výzkumný ústav anorg. chemie, Ústí nad Labem, Czechoslovakia). *Chem. Průmysl*, 1956, **6** (4), 143–145.—A recording apparatus for the continuous polarographic determination of SO_2 in waste gases has been devised; it consists of a polarograph and a simple gas absorber with a continuous constant-rate flow of electrolyte (0·1 *N* H_2SO_4). A study of the influence of a number of factors on the accuracy of the determination has shown that the height of the limiting current is a linear function of SO_2 concn., decreasing with an increasing rate of flow of the electrolyte. Sulphur trioxide can be present without interference. The results agree with those obtained iodimetrically. G. GLASER

3243. **Oscillographic polarography. I. An improved apparatus for the observation of current-voltage, reduction and re-oxidation patterns.** Mutsuaki Shinagawa, Hideo Imai and Shokichi Chaki (Fac. Sci., Hiroshima Univ., Hiroshima). *J. Electrochem. Soc. Japan*, 1955, **23** (3), 132–135.—Modifications of the Ševčík apparatus (*Coll. Czech. Chem. Commun.*, 1948, **113**, 314) were suggested for the study of the control of duration of reduction and re-oxidation and of initial sweep voltage. For the latter, the use of a differential amplifier for the horizontal axis was recommended. The control can be achieved by applying optional triangular sweep voltage and by compensating the d.c. voltage, on which the triangular voltage imposes, with the aid of a potentiometer circuit. Sweep frequency is easily controlled and the fluctuation of the output voltage is minimised by a voltage chopper. For the measurement of the current, a precision variable resistor is used as a potentiometer which functions as a sensitivity control.

II. Characteristics of the apparatus in operation. Mutsuaki Shinagawa and Hideo Imai. *Ibid.*, 1955, **23** (4), 187–190.—Several characteristic features in the operation of the new apparatus were examined, including (*i*) the effect of sweep voltage span and of the initial voltage on the relation of the wave height with the duration of reduction and re-oxidation, (*ii*) the influence of the variation of the drop time of the mercury electrode on the wave height, and (*iii*) the influence of max. suppressor and of dissolved oxygen on some ions, such as Cd, Zn and Pb.

III. The characteristics of the peak current and the peak potential of an irreversible depolariser. Hideo Imai. *Ibid.*, 1955, **23** (10), 530–536.—The characteristics of the peak current and the peak potential of irreversible polarographic waves were studied with reference to the non-linearity of the current-concn. diagram. Examples were provided by the observation of the polarographic waves of Zn, Cd, Pb, Tl^{I}, In^{III}, Ni and Co in various supporting electrolytes. The decrease in the depolarising current on the application of potential change at a high rate is discussed and the origin of experimental error for the measurement of reduction potential of various ions in the mixed soln. is suggested.

IV. The influence of the initial sweep voltage and the mercury head on the irreversibility of the depolariser. Hideo Imai. *Ibid.*, 1955, **23** (11), 583–588.—The change in the peak current due to the change of the initial sweep voltage and of the mercury head is discussed with irreversible depolarisers by the use of either a dropping or stationary electrode. When the initial sweep voltage is shifted to a more negative potential with a high rate of potential change, the decrease in peak current shows a similar trend to that of the re-oxidation period. The re-oxidation of Zn is incomplete and the concn. of the oxidised form on the surface of the electrode decreases so that a hysteresis effect is observed. K. SAITO

3244. **Apparatus for automatic titration [by the potentiometric method].** Beckman Instruments, Inc. (Assignees of R. C. Hawkes and A. Strickler) (820 Mission Street, South Pasadena, Calif., U.S.A.), Brit. Pat. 749,572; Date appl., 19.11.51. U.S.A., 3.3.51.—An automatic titrator, usable with conventional burettes, comprises a control valve whereby the titrant is delivered continuously to the sample until the end-point is almost reached, whereupon the delivery of the titrant becomes intermittent. To the generated electrode potential a supplementary electrical potential, of progressively decreasing effect, is added to produce a series of false end-point arrival signals, with corresponding hesitations in delivery before the actual predetermined end-point potential is reached. J. M. JACOBS

3245. **Stable high-frequency titration apparatus in the 100-Mc. frequency range.** A. H. Johnson and A. Timnick (Mich. State Univ., East Lansing, U.S.A.). *Anal. Chem.*, 1956, **28** (5), 889–892.—By modifying the high-frequency titrimeter described by Anderson *et al.* (*Brit. Abstr. C*, 1950, 466), the operating frequency can be extended to 130 megacycles per sec. The multi-turn coil is replaced by a co-axial half-wave line, and the cell is designed as a capacitor, *i.e.*, the plates are in contact with the walls of the titration vessel. By following the oscillator-tube grid-current change polarographically, response curves can be obtained for 0·001 to 1 *M* NaCl and for 0·0001 to 0·04 *M* $HClO_4$ in glacial acetic acid, operating at 130 megacycles per sec. The titration curves are more linear at 120 megacycles per sec., thus facilitating location of the end-point. W. J. BAKER

3246. **Neutron activation analysis for trace elements.** G. H. Morrison (Sylvania Electric Products, Inc., Flushing, N.Y., U.S.A.). *Applied Spectroscopy*, 1956, **10** (2), 71–75.—General procedures, involving the bombardment of the sample in a high-flux nuclear reactor, followed by chemical separation of the required impurity isotopes and their estimation by a Geiger counting technique, are discussed. Comparative sensitivities of a number of elements are given. Gamma scintillation spectrometry, with a thallium-activated sodium iodide crystal viewed by a photomultiplier, eliminates the need for chemical separation. Results of the application of this technique to the estimation of impurities in crystals of Si, and of Cu and Cr in aluminium alloys are given. A standard deviation of about 1 per cent. of content was obtained for Cr at 0·03 per cent. and for Cu at 0·29 per cent. levels. P. T. BEALE

See also Abstract 3210.

ERRATUM.—March (1956) issue, abstract 842, line 3. *For* "1955" *read* "1954".

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångstrom unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher, -e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
critical	crit.
crystalline, crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c.p.s.
decompos -ing, -ition	(decomp.)
density	ρ
density, relative	d or wt. per ml
derivative	deriv.
dilute	dil.
direct current	d.c.
distilled	dist.
electromotive force	e.m.f.
electron-volt	eV
equivalent	equiv.
experiment	expt.
foot, feet	ft.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
horse-power	h.p.
hour	hr.
hydrogen ion concentration	$[H^{\cdot}]$
hydrogen ion exponent	pH
inch	in.
infra-red	i.r.
insoluble	insol.
kilogram	kg
kilovolt	kV
kilowatt	kW
maxim -um, -a	max.
melting-point	m.p.
microcurie	μC
microgram	μg
microlitre	μl
micron	μ
milliampere	mA
millicurie	mC
milligram	mg
millilitre	ml
millimetre	mm
millimicron	mμ
millivolt	mV
minimum	min.
minute (time)	min.
molar (concentration)	M
molecul -e, -ar	mol.
normal (concentration)	N
number	no.
observed	(obs.)
ounce	oz
part	pt.
patent	pat.
parts per million	p.p.m.
per cent. wt. in wt.	per cent. w/w
per cent. wt. in vol.	per cent. w/v
per cent. vol. in vol.	per cent. v/v
potential difference	p.d.
pound	lb
precipitate	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n^t_λ
relative humidity	R.H.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]^t_\lambda$
square centimetre	sq. cm
standard temperature and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition the following symbols are used—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicles are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, *e.g.*, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, Cl', SO_4''. Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, *e.g.*, ferric iron becomes Fe^{III} and cuprous copper Cu^{I}.

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